Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Synthesis and structural chemistry of bicyclic hexaaza-dithia macrocycles containing pendant donor groups

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Supporting Information

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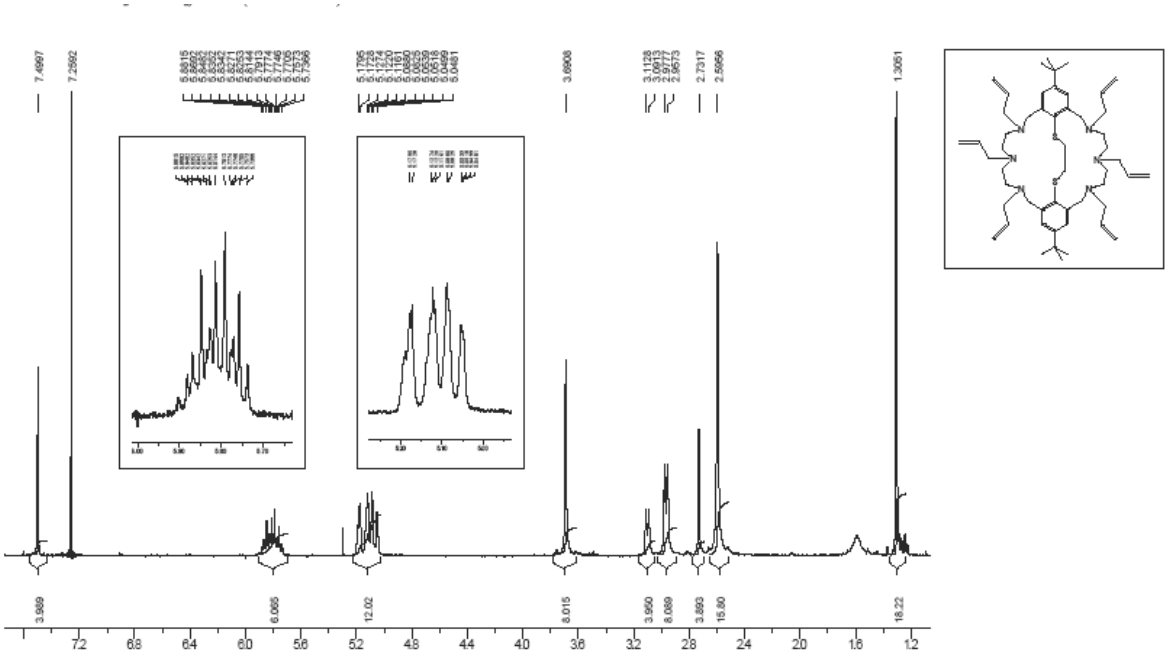
1. Spectra for hexaallylated aza-thioether **8**.



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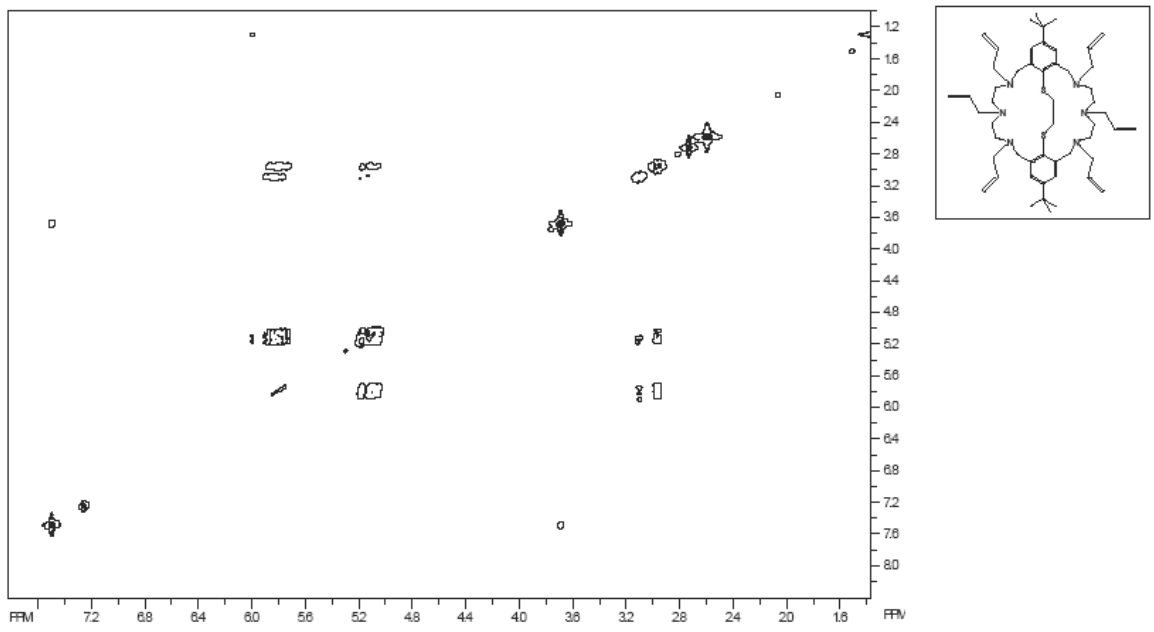

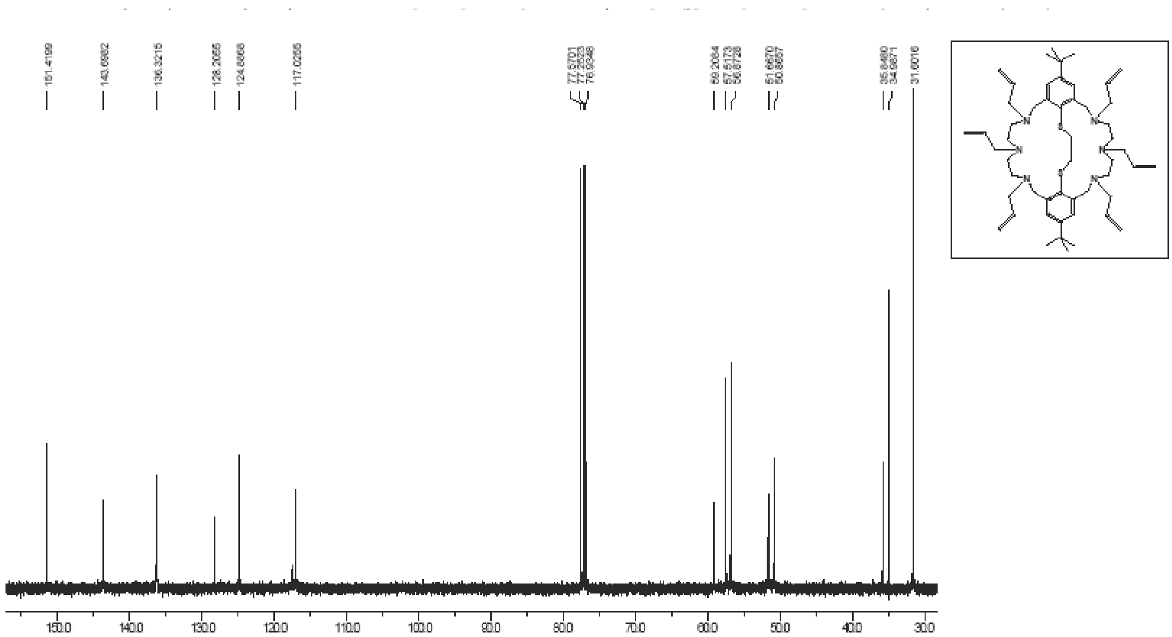
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124.8868
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77.2523
76.9348
59.2064
57.5173
56.8728
51.6670
50.6657
35.8480
34.9871
31.6016
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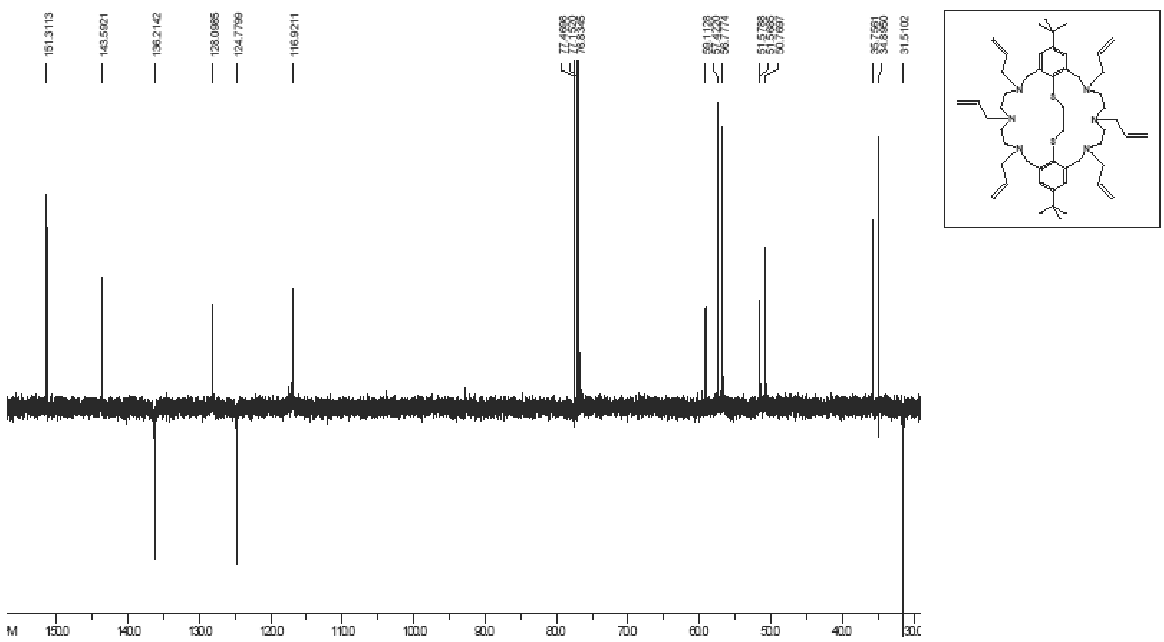
APT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136.2142
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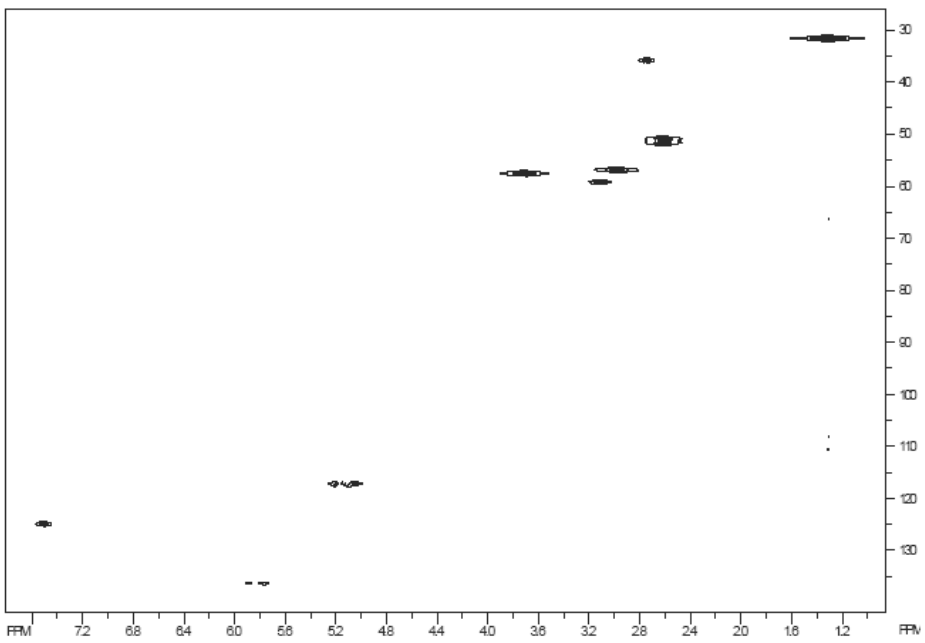
124.7799
116.9211
77.4688
77.1520
76.8345
59.1128
57.4220
56.7774
51.5788
51.5665
50.7697
35.7561
34.8950
31.5102
150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0

HSQC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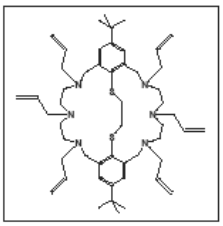
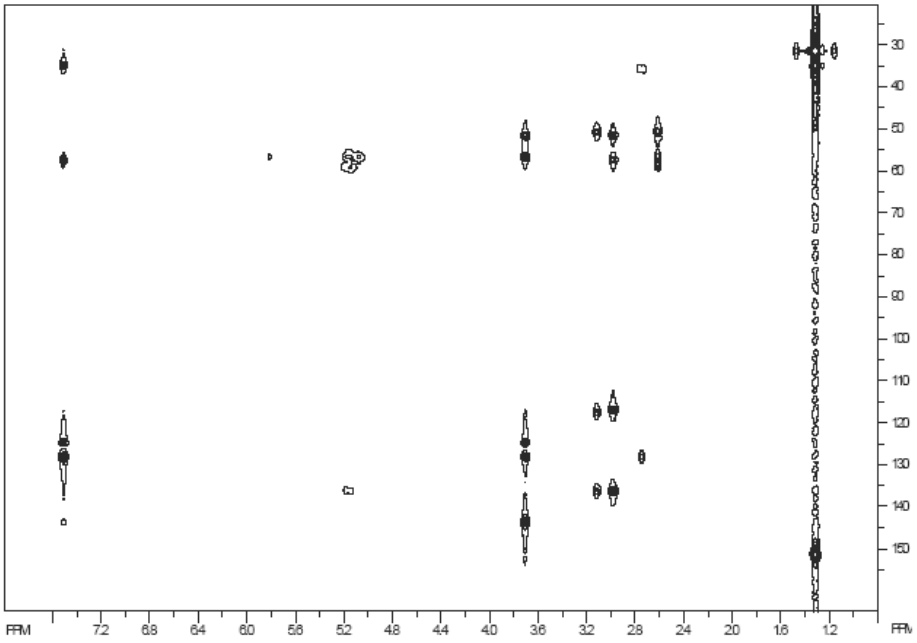
40
50
60
70
80
90
100
110
120
130
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM



HMBC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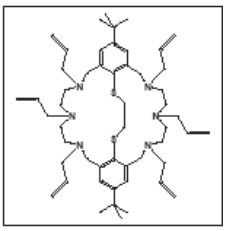
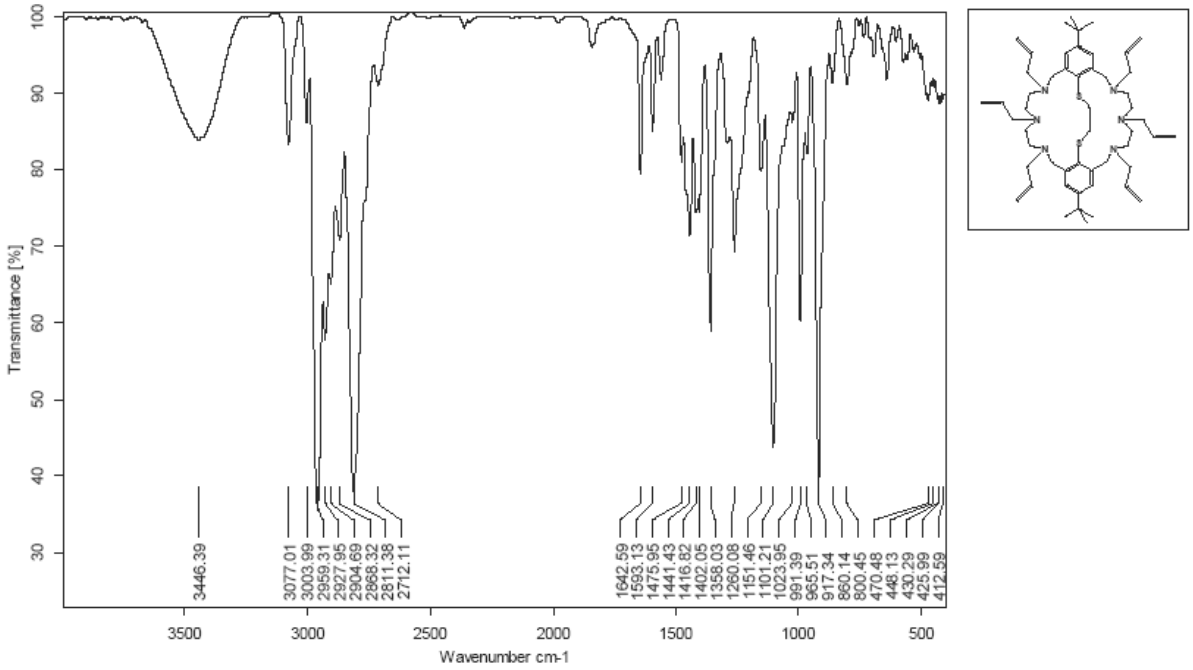
60
70
80
90
100
110
120
130
140
150
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM



IR- Spektrum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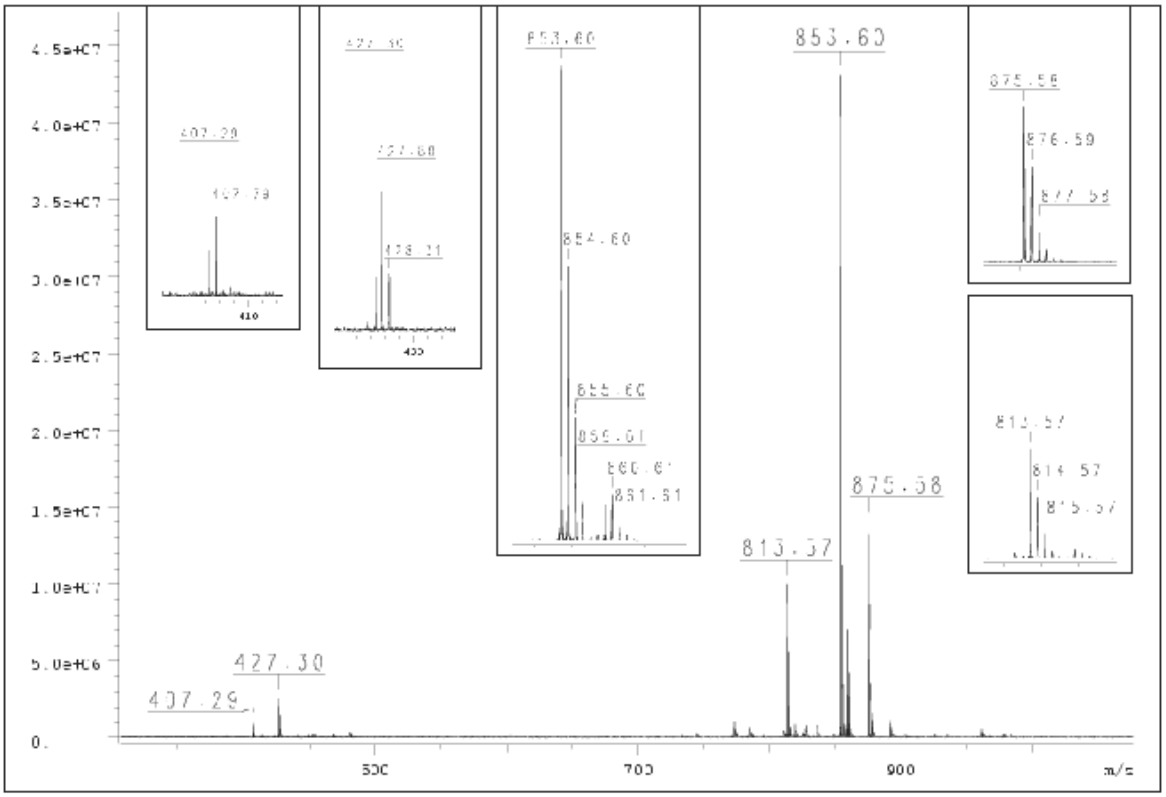
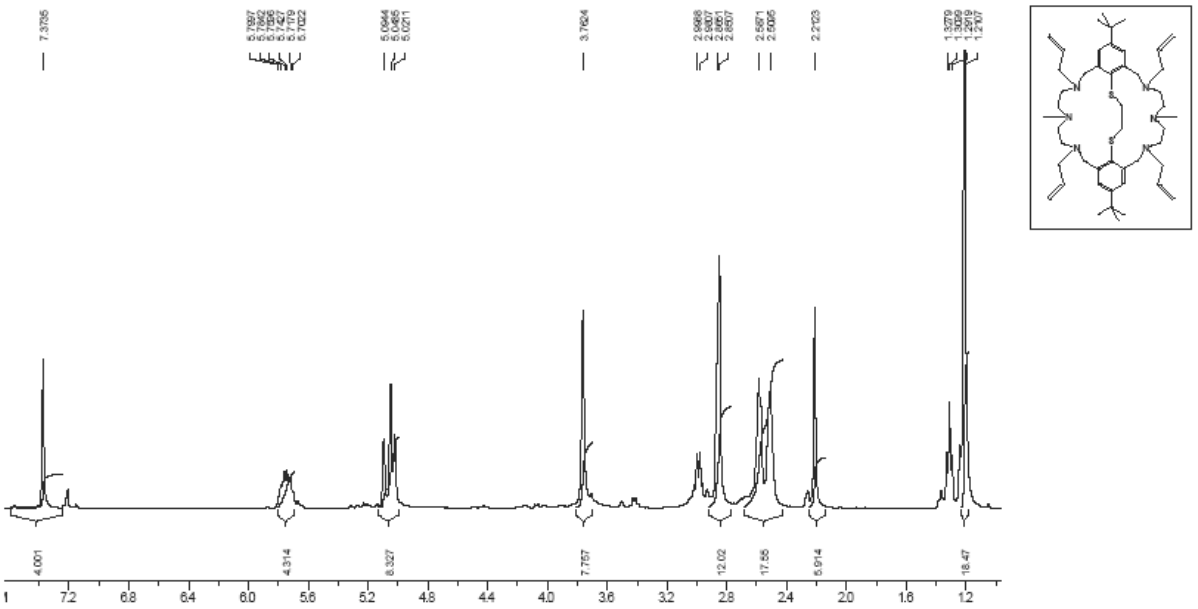
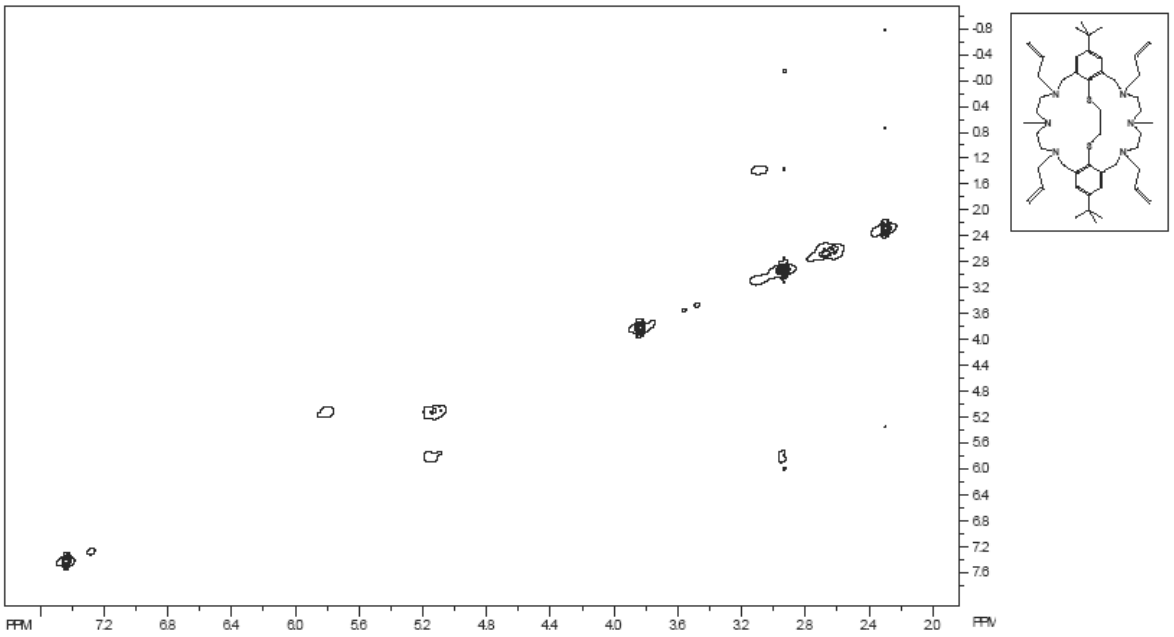
3077.01
3003.99
2959.31
2927.95
2904.69
2868.32
2811.38
2712.11
1642.59
1593.13
1475.95
1441.43
1416.82
1402.05
1358.03
1260.08
1151.46
1101.21
1023.95
991.39
965.51
917.34
860.14
800.45
470.48
448.13
430.29
425.99
412.59

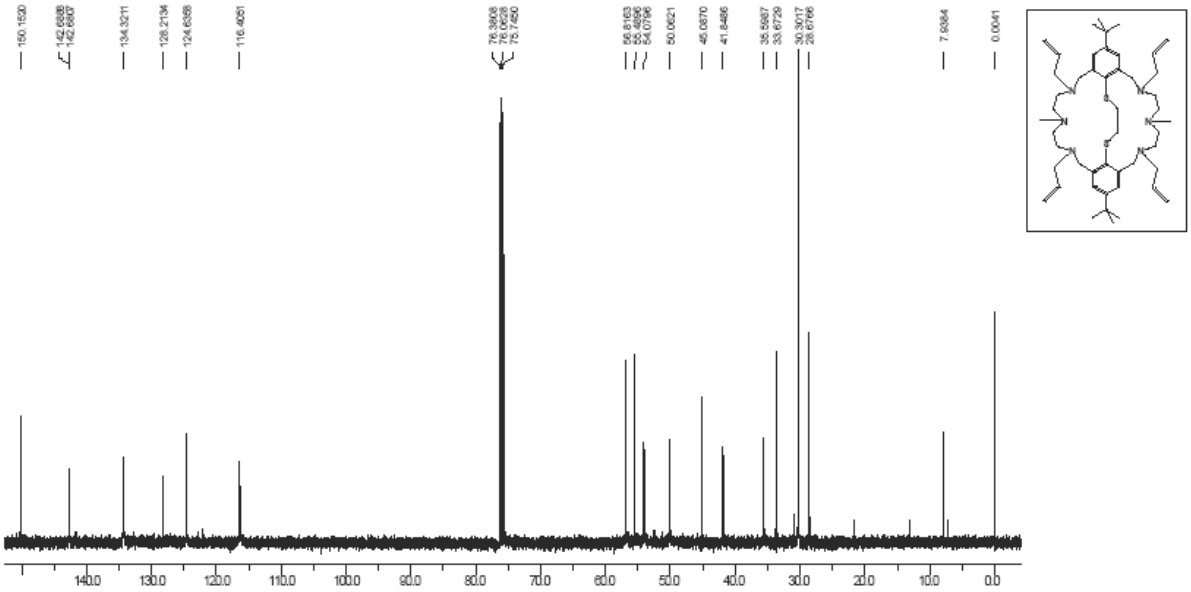

853.60
875.58
813.57
427.30
427.29
m/z

2. Spectra for tetraallylated aza-thioether **9**.



$^1H/^1H$- COSY

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142.6888
142.6807
134.3211
128.2134
124.6388
116.4061
76.3808
76.0628
75.7450
56.8163
55.4958
54.0796
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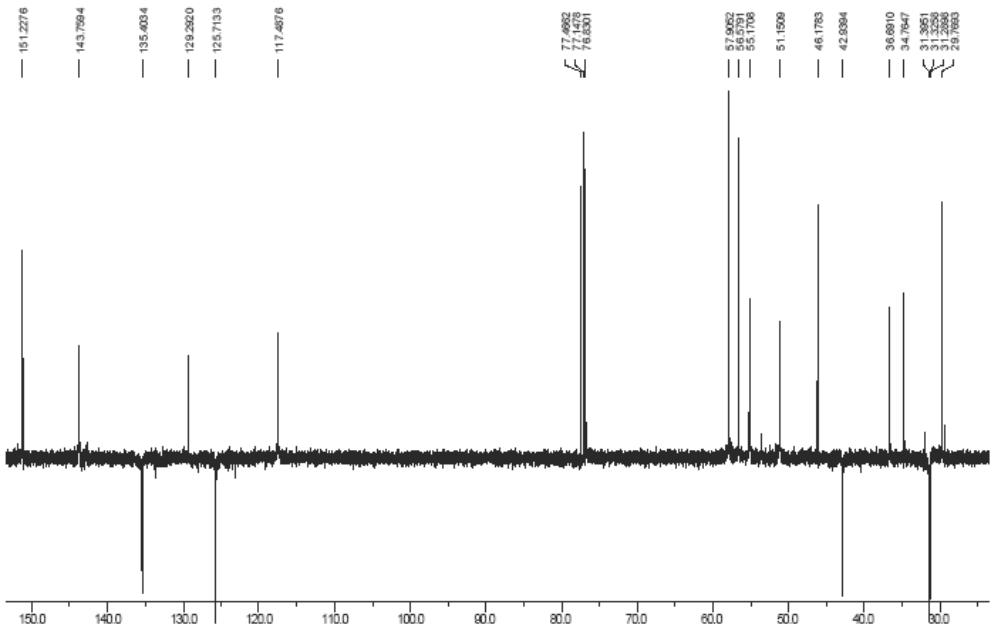
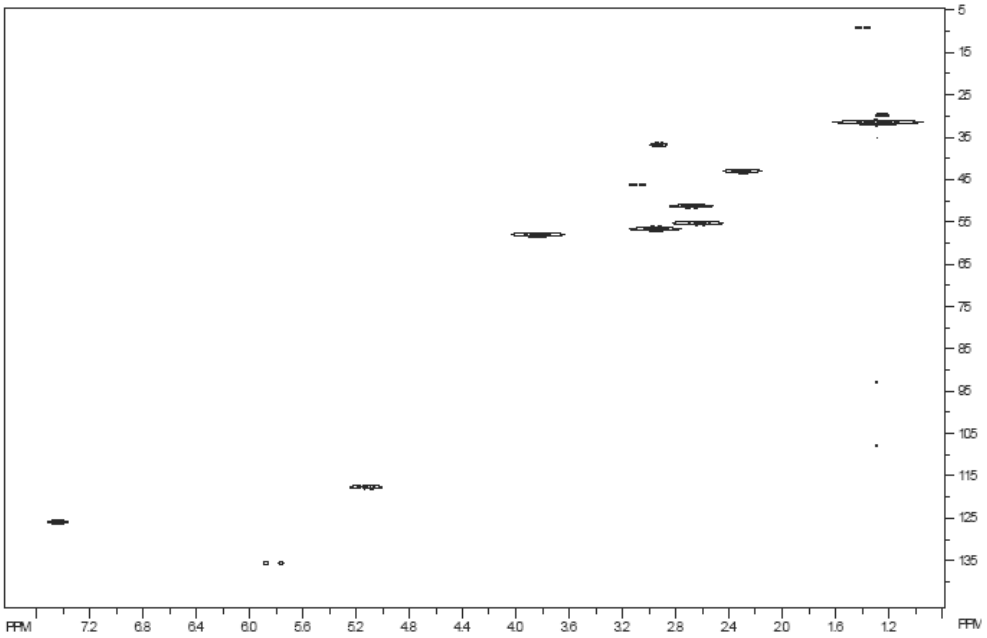
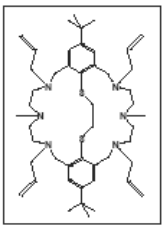
30.3017
28.6766
7.6384
0.0041

APT

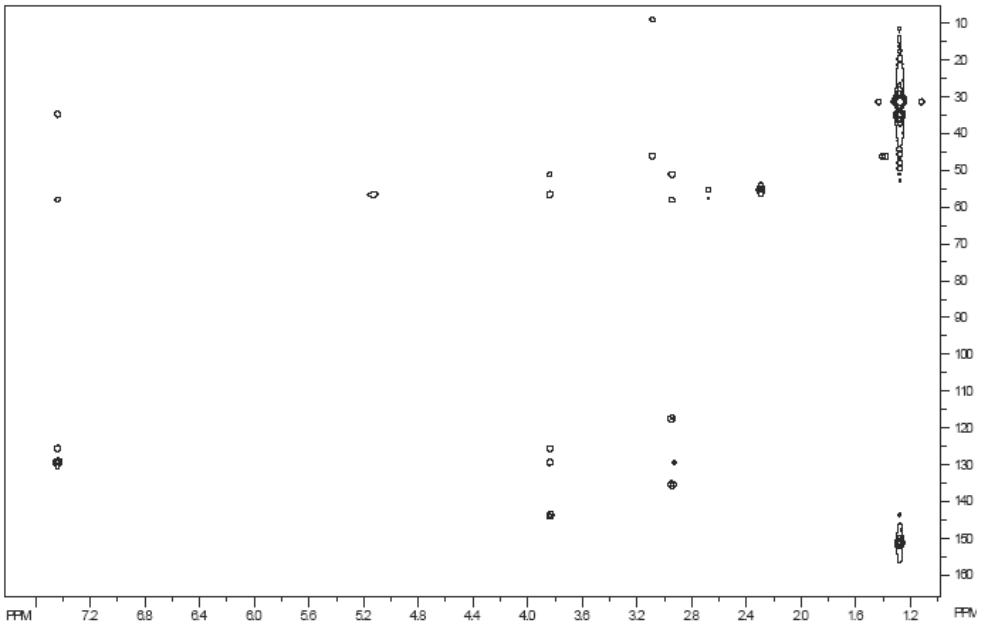

151.2276
143.7994
135.4034
129.2920
125.7133
117.4878
77.4682
77.1478
76.8301
57.9052
55.8701
55.1709
51.1509
46.1783
42.9394
36.8910
34.7647
31.3951
31.3555
31.2866
29.7693

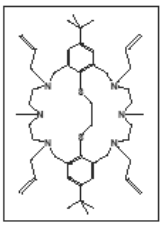
HSQC


5
15
25
35
45
55
65
75
85
95
105
115
125
135
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM



HMBC


10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM



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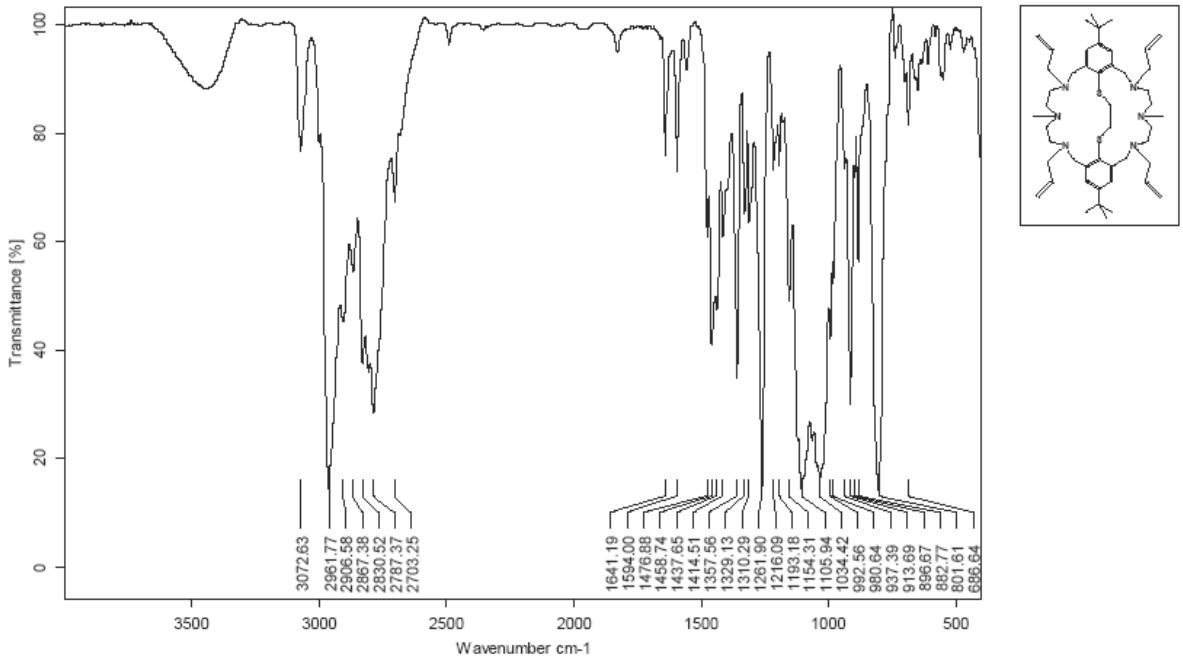
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Wavenumber cm-1
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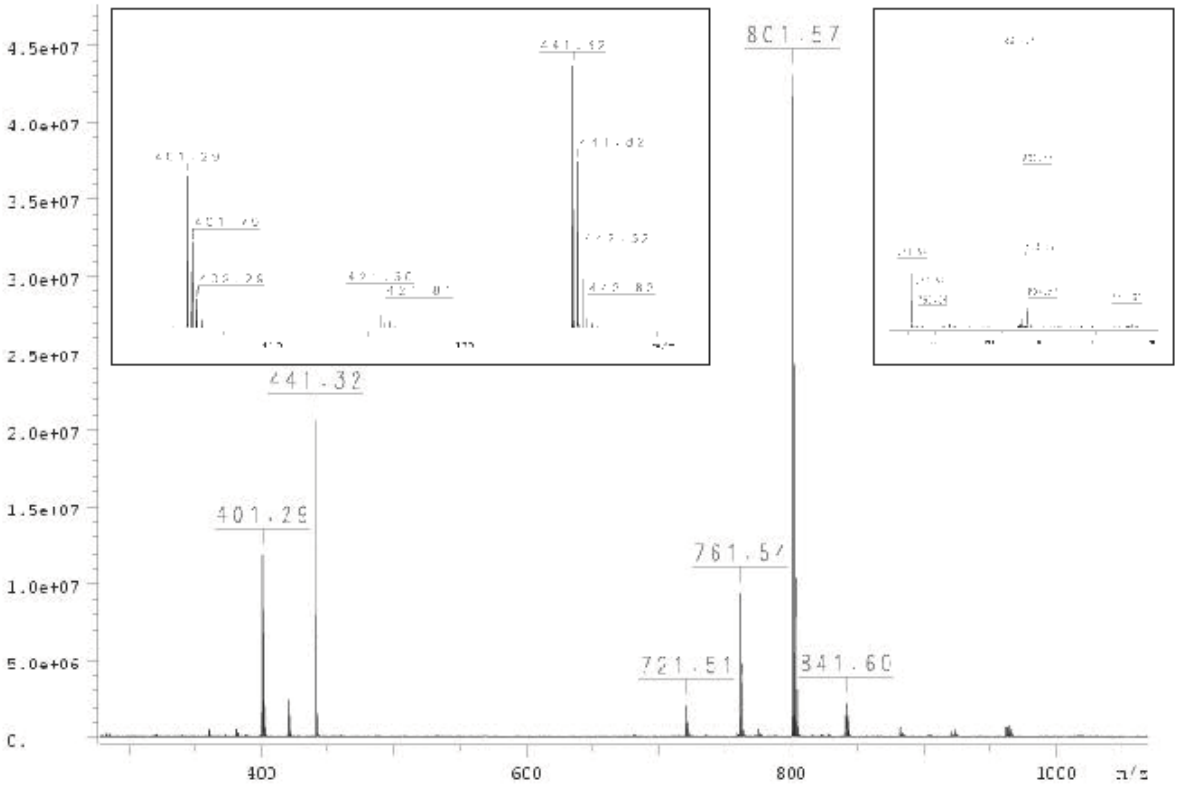
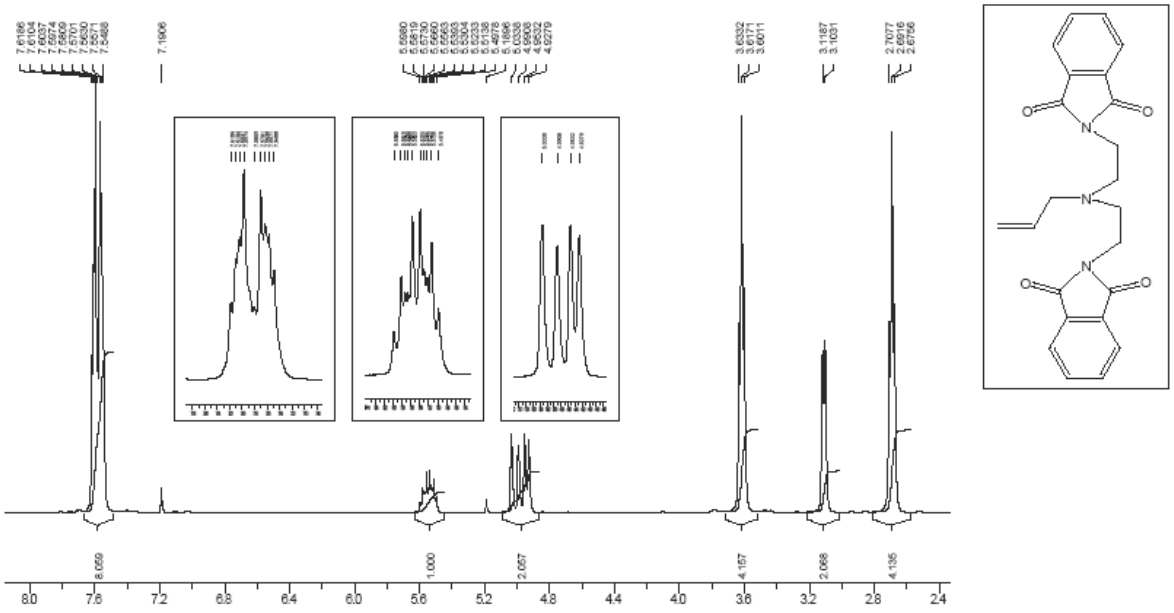
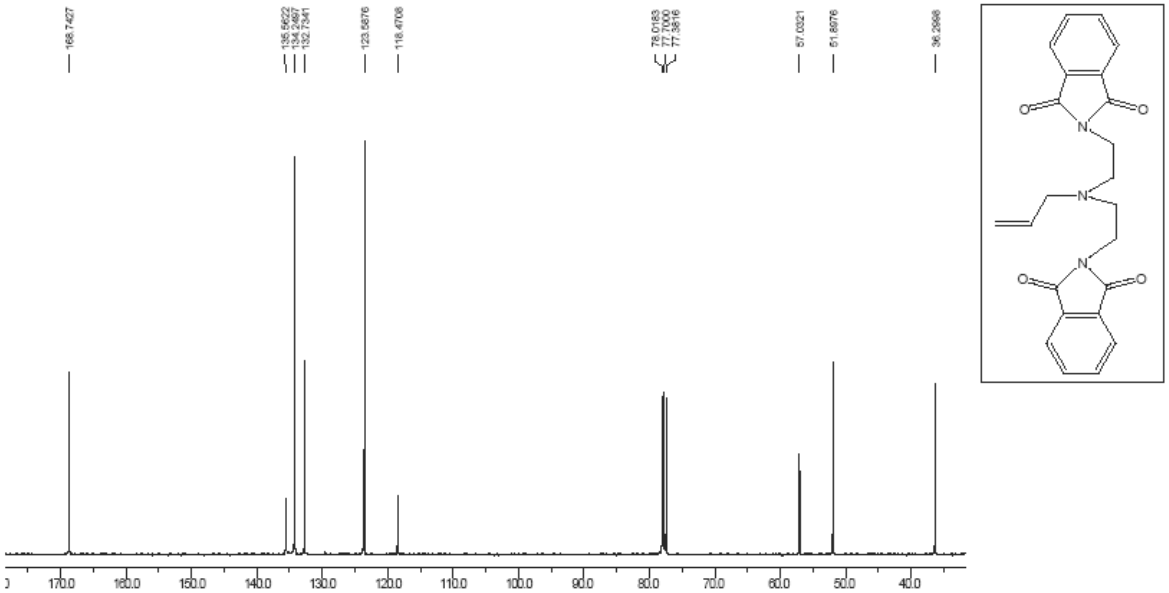
2906.58
2867.38
2830.52
2787.37
2703.25
1641.19
1594.00
1476.88
1458.74
1437.65
1414.51
1357.56
1329.13
1310.29
1261.90
1216.09
1193.18
1154.31
1105.94
1034.42
992.56
980.64
937.39
913.69
896.67
882.77
801.61
686.64


801.57
441.32
401.29
761.54
721.51
841.60
m/z

3. Spectra for N-Allyl-bis(2-phthalimidoethyl)amine **12**.





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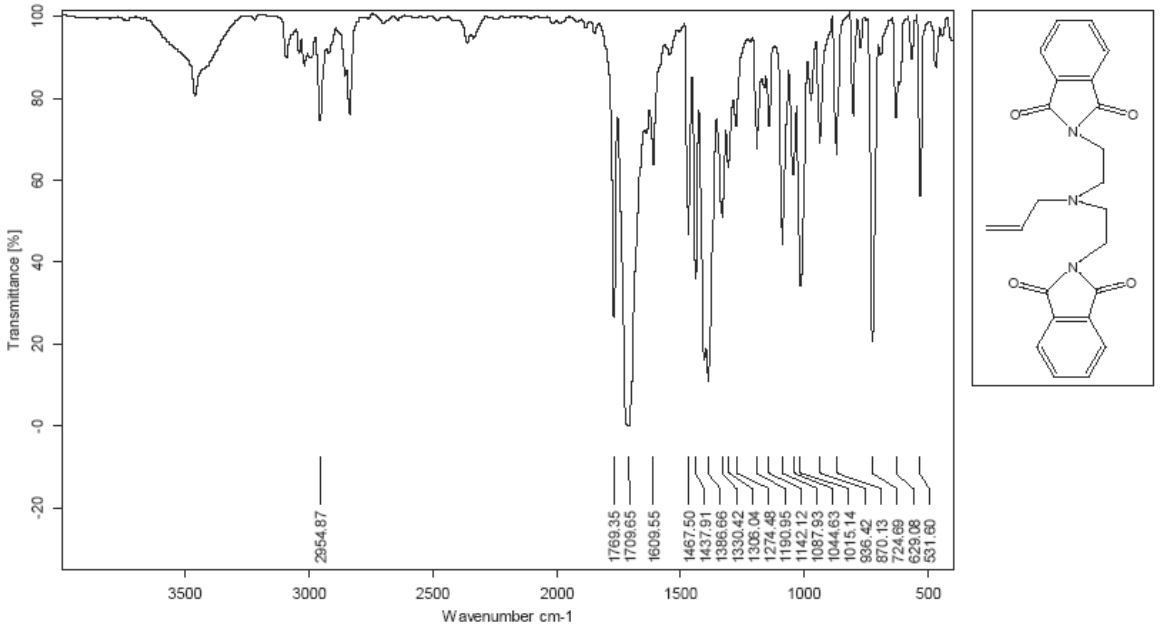
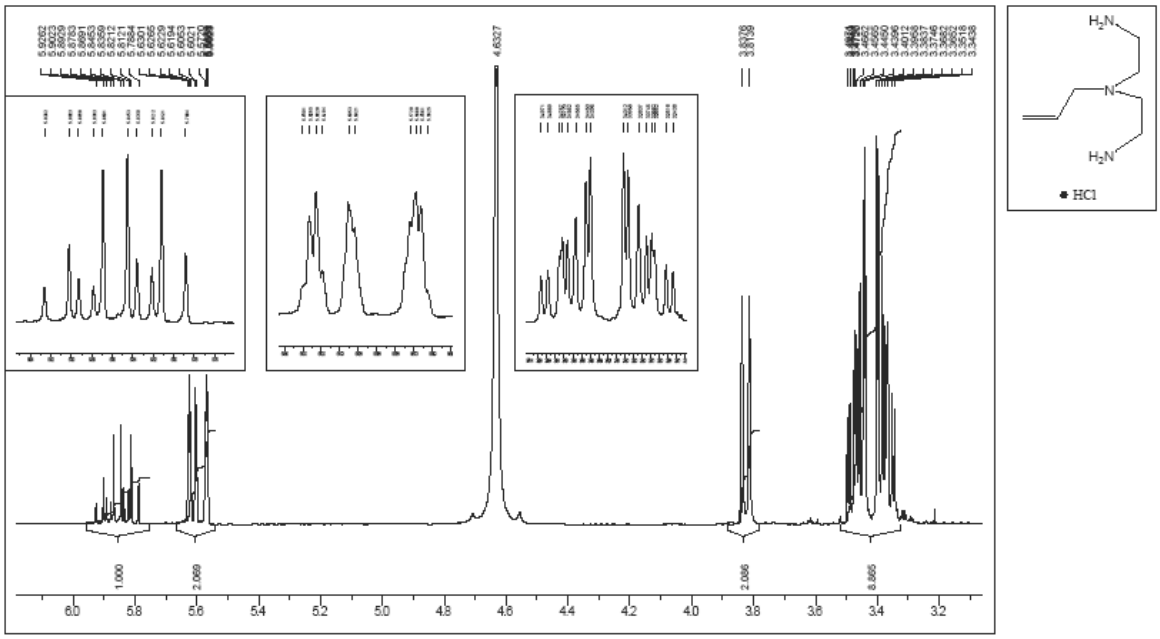
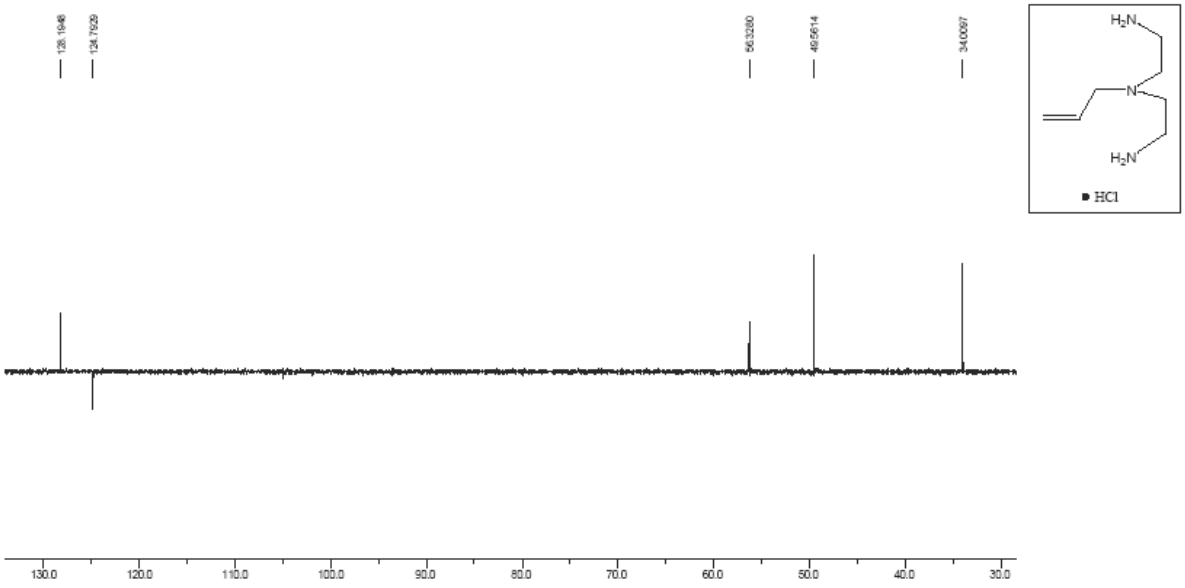

Transmittance [%]
100
80
60
40
20
-0
-20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
2954.87
1769.35
1709.65
1609.55
1467.50
1437.91
1386.66
1330.42
1305.04
1274.48
1190.95
1142.12
1087.93
1044.63
1015.14
936.42
870.13
724.69
629.08
531.60
O
O
N
N
N
O
O

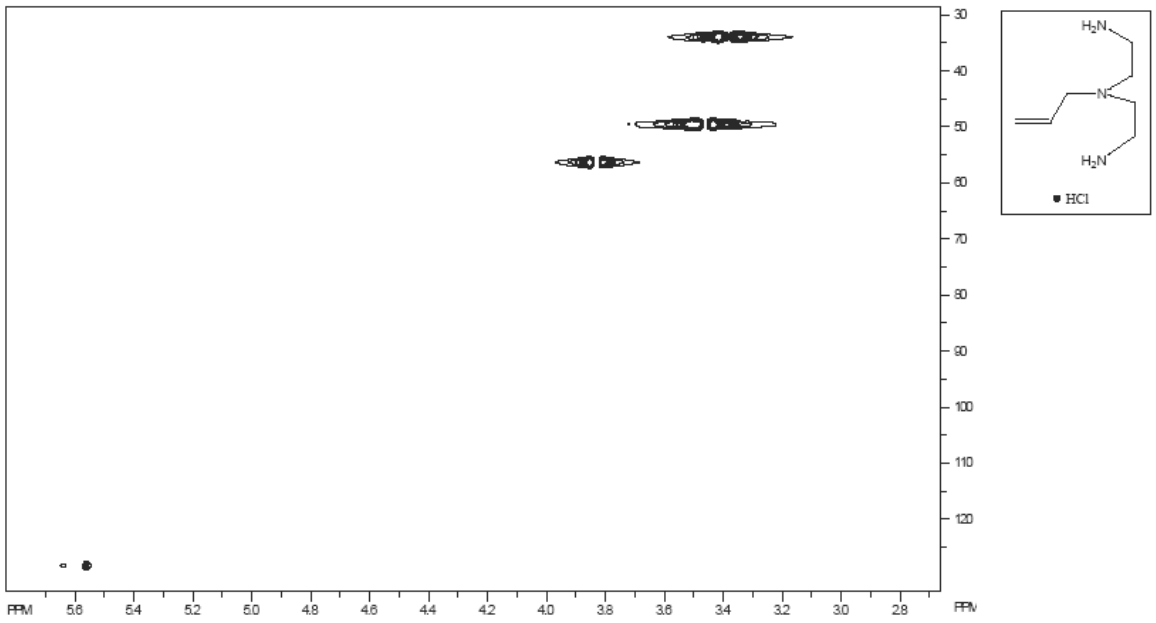
4. Spectra for N-Allyl-bis(2-aminoethyl)amine trihydrochloride (**13**·3HCl).



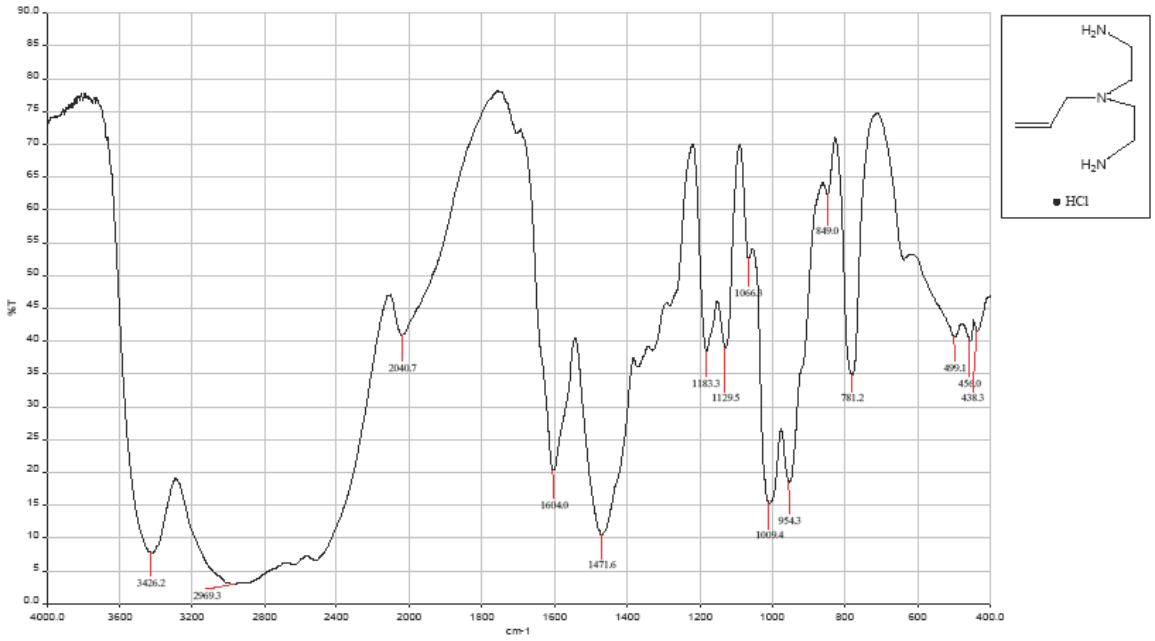
APT (100 MHz, D_2O): δ (ppm)= 34.0 [s, 2 C, $(H_2NCH_2CH_2)_2NCH_2CHCH_2$], 49.6 [s, 2 C, $(H_2NCH_2CH_2)_2NCH_2CHCH_2$], 56.3 [s, 1 C, $(H_2NCH_2CH_2)_2NCH_2CHCH_2$], 124.8 [s, 1 C, $(H_2NCH_2CH_2)_2NCH_2CHCH_2$], 128.2 [s, 1 C, $(H_2NCH_2CH_2)_2NCH_2CHCH_2$].



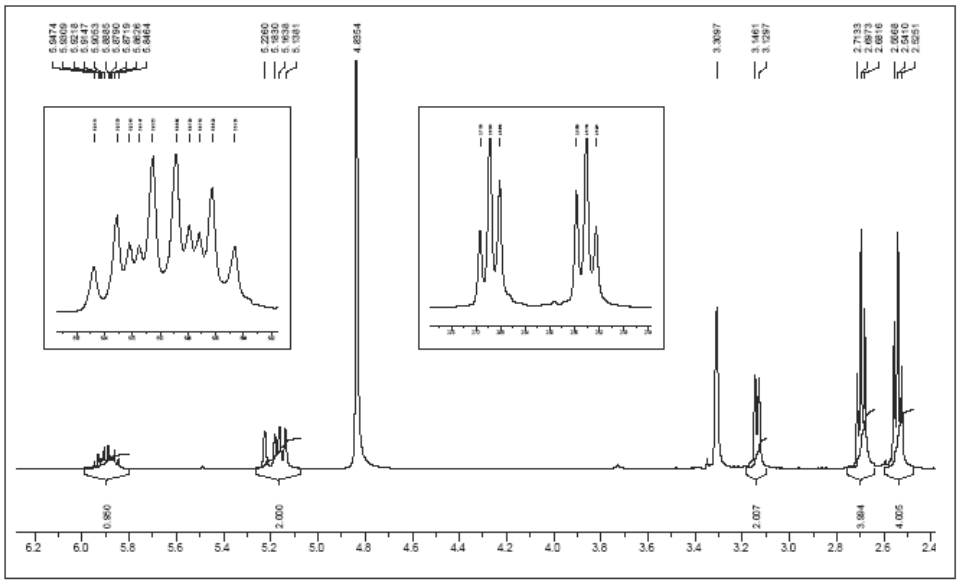
HSQC

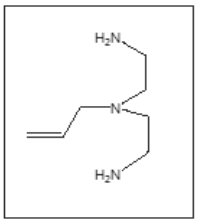


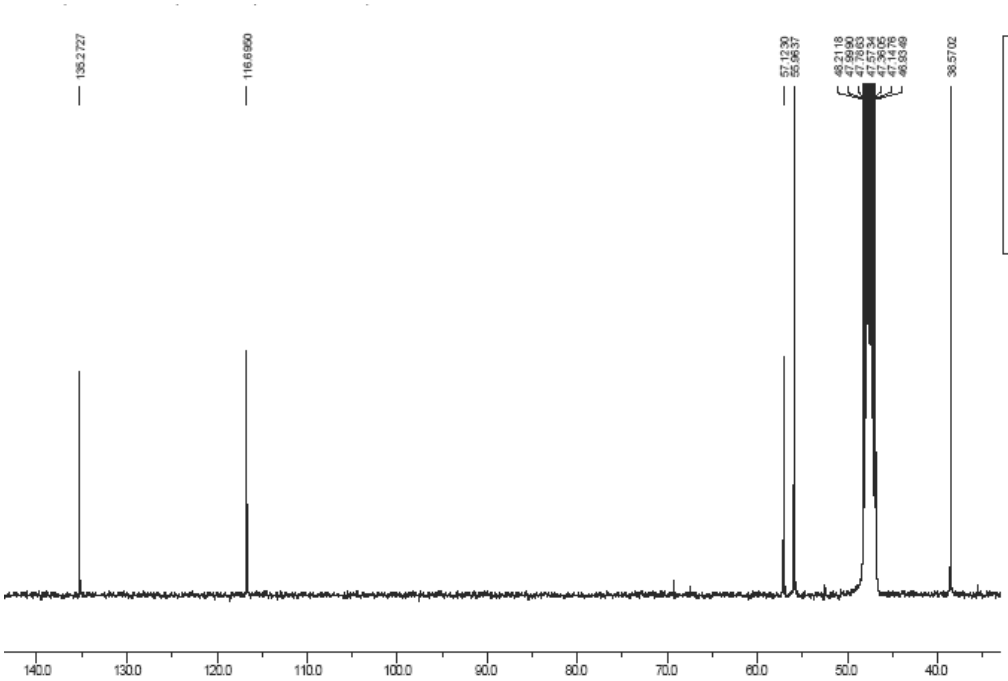
IR-Spektrum

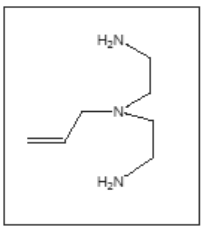


5. Spectra for N-allyl-bis(2-aminoethyl)amine **13**·0.5H_2O.

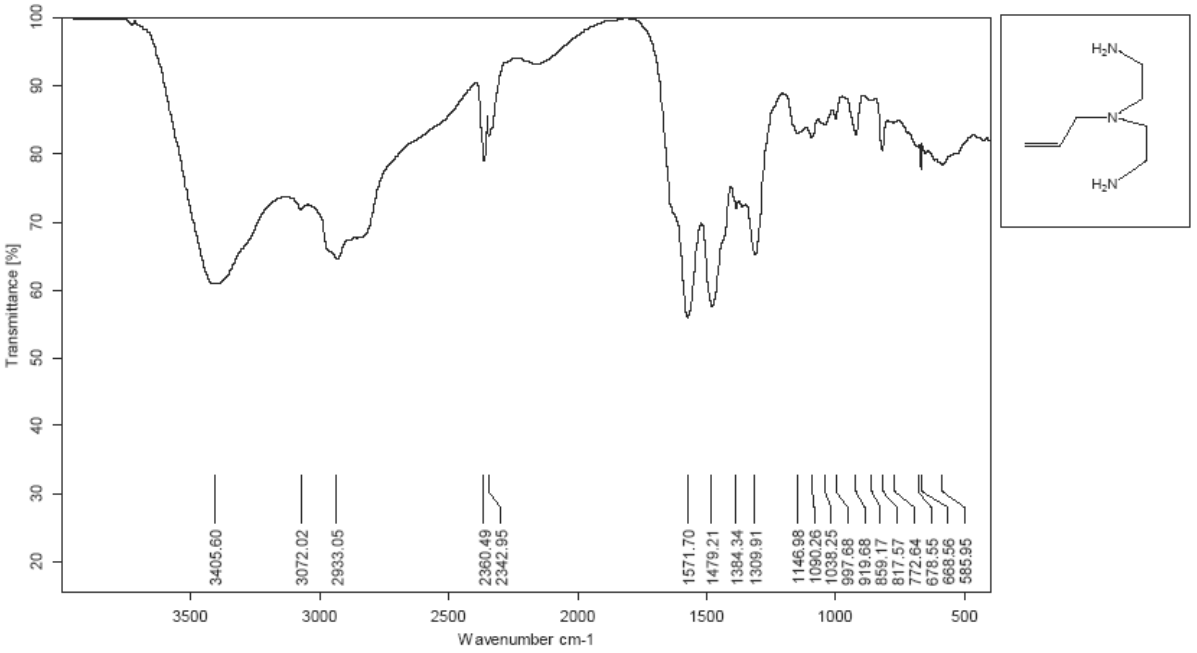








IR-Spektrum


Transmittance [%]
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70
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30
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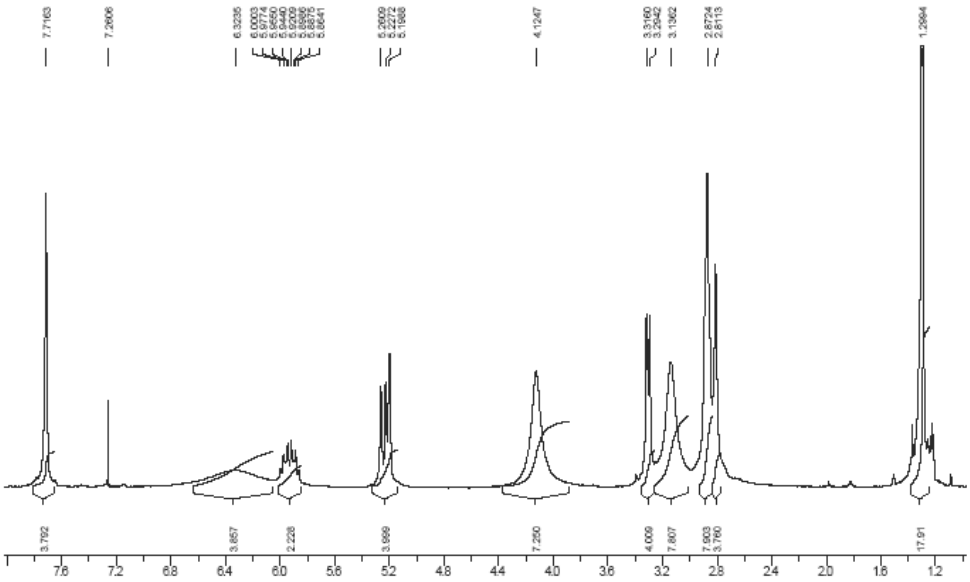
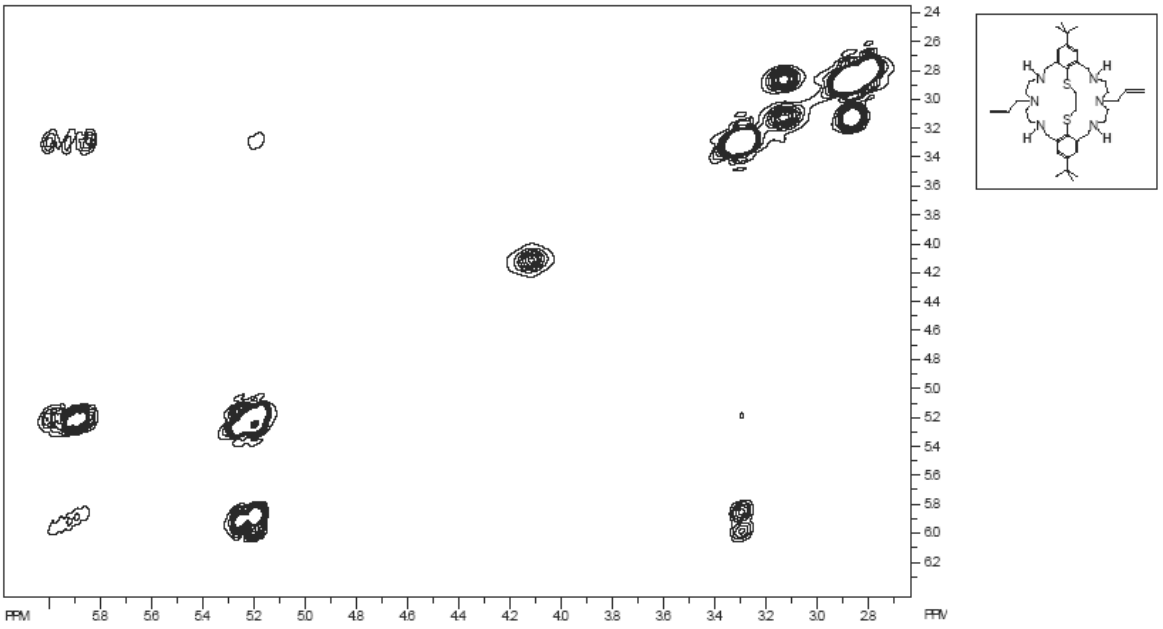
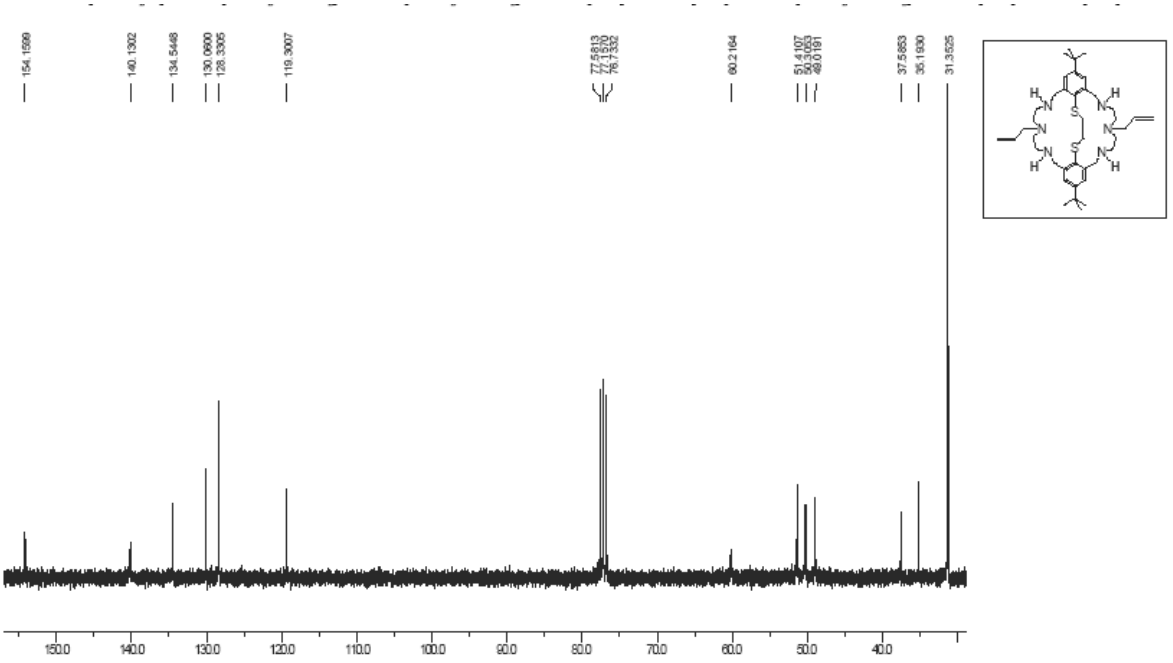
2933.05
2360.49
2342.95
1571.70
1479.21
1384.34
1309.91
1146.98
1090.26
1038.25
997.68
919.68
859.17
817.57
772.64
678.55
668.56
585.95
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
H2N
N
H2N

6. Spectra for bis-allylated aza-thioether **14**.

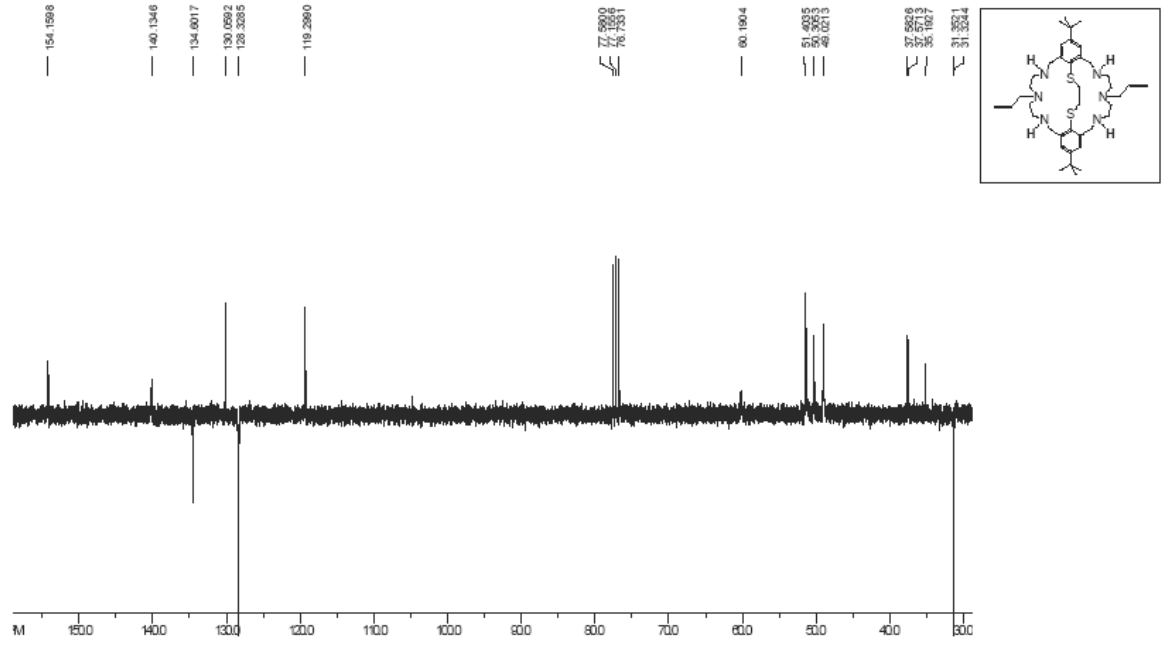


$^{1}H/^{1}H$-COSY

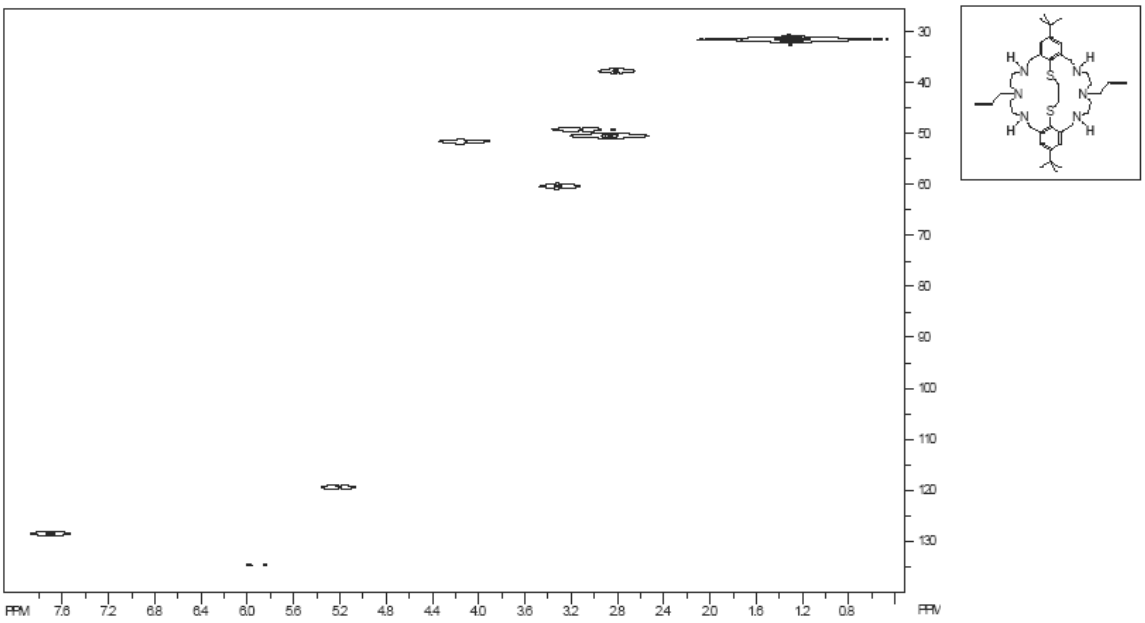



154.1599
140.1302
134.5448
130.0690
128.3305
119.3007
77.5813
77.1590
76.7332
60.2164
51.4107
50.3053
49.0191
37.5853
35.1930
31.3525

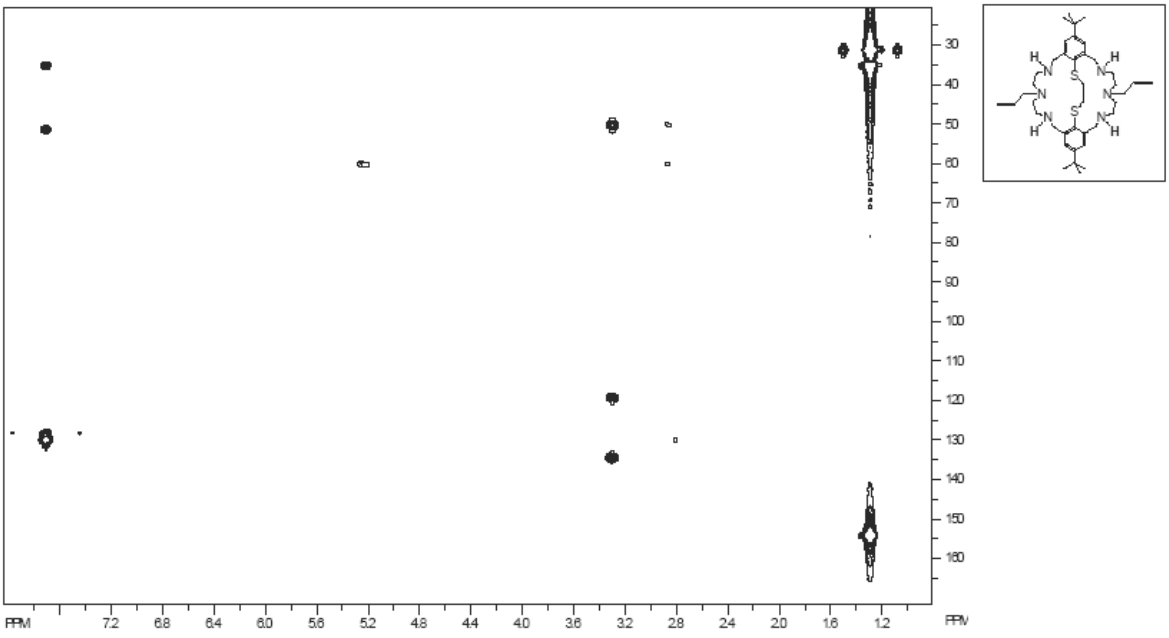
APT


154.1598
140.1346
134.6017
130.0592
128.3285
119.2980
77.5800
77.1588
76.7331
60.1904
51.4035
50.3053
49.0213
37.5826
37.5713
35.1927
31.3521
31.3324

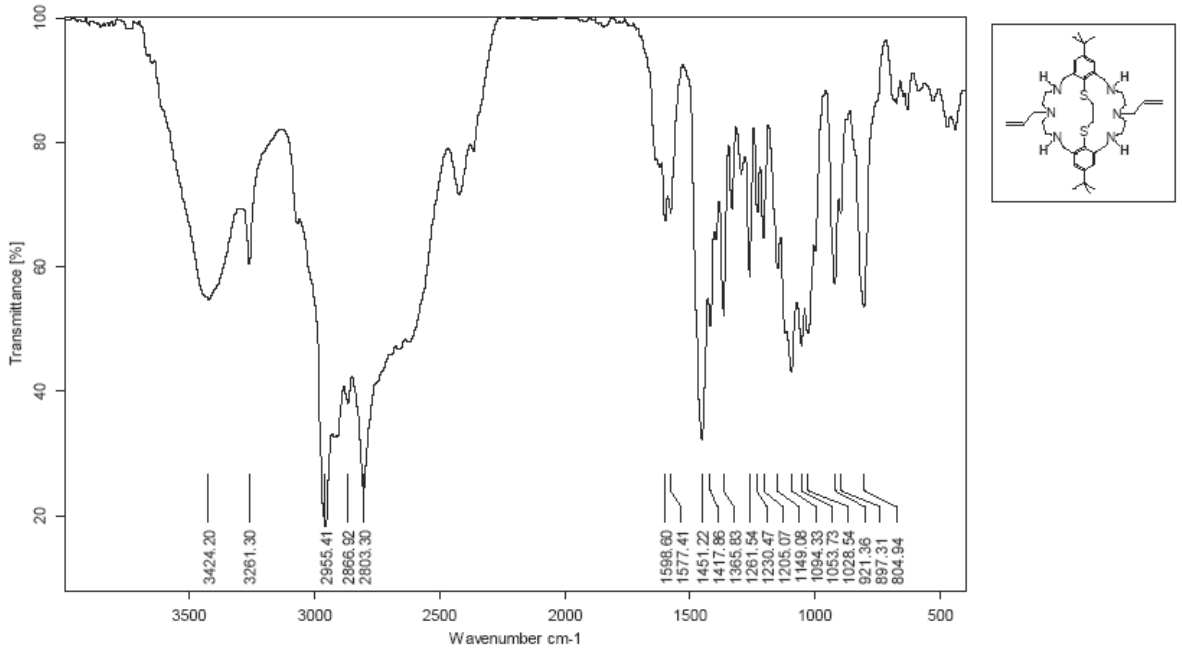
HSQC


30
40
50
60
70
80
90
100
110
120
130
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
PPM

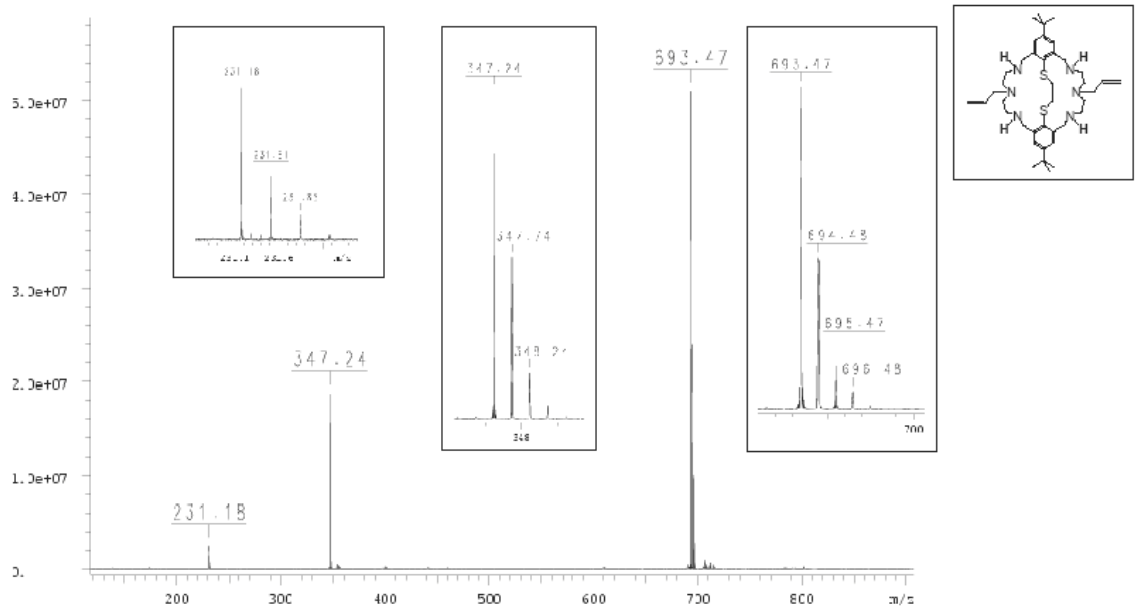
HMBC


30
40
50
60
70
80
90
100
110
120
130
140
150
160
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM

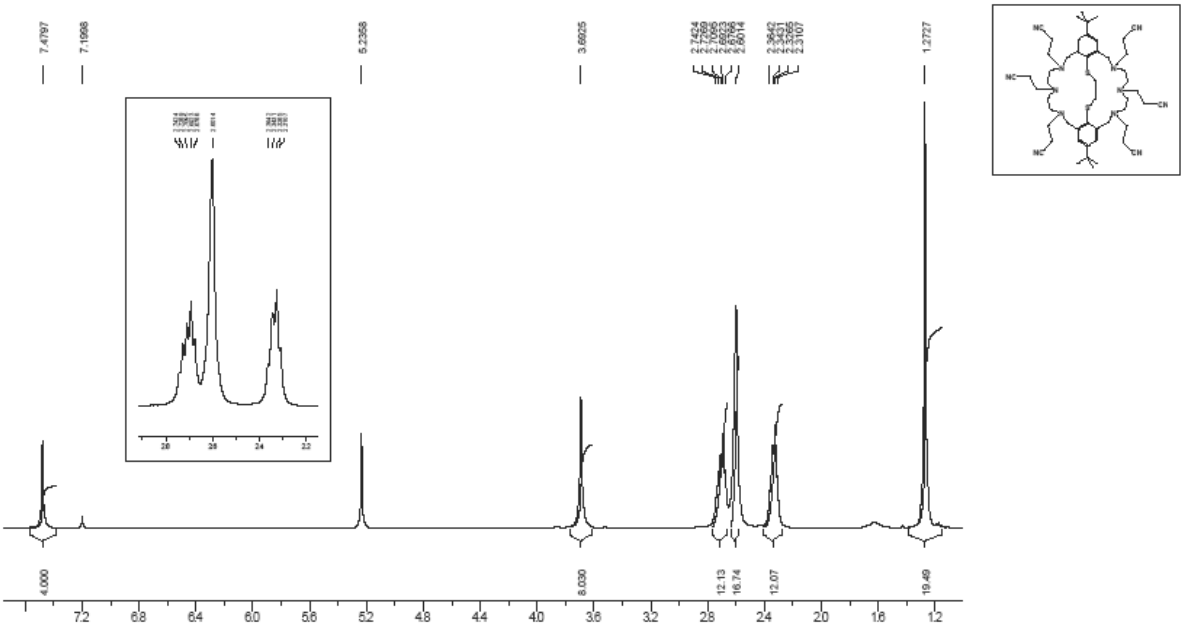
IR-Spektrum



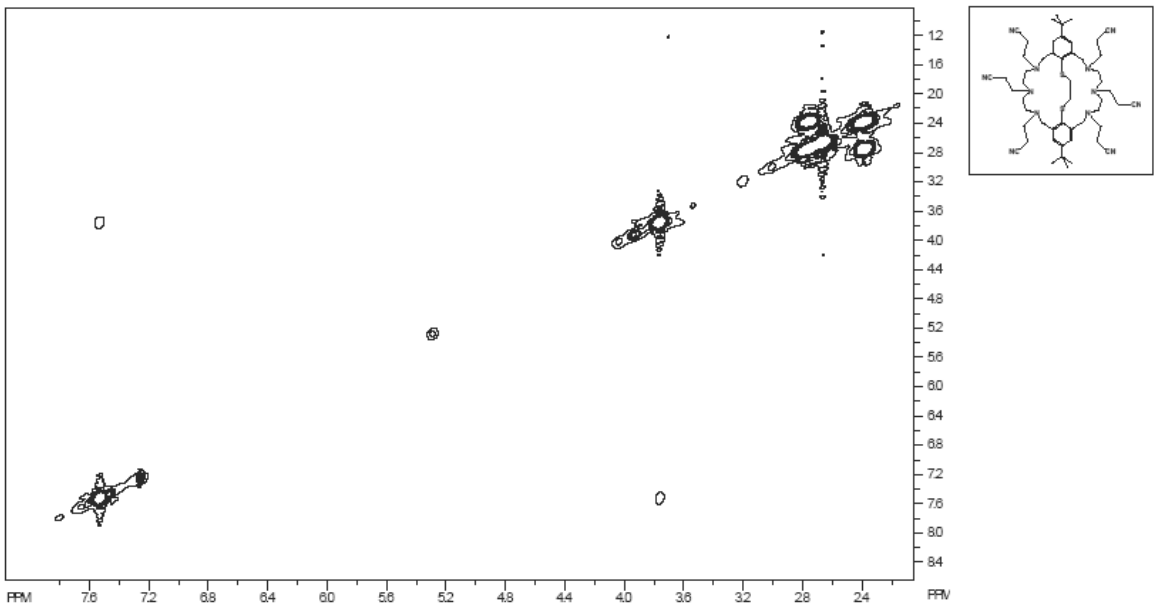
MS (ESI, positiv, CH_3OH): m/z= 231.18 ($C_{40}H_{64}N_6S_2$ +3H$^+$), 347.24 ($C_{40}H_{64}N_6S_2$ +2H$^+$), 693.47 ($C_{40}H_{64}N_6S_2$ +H$^+$).

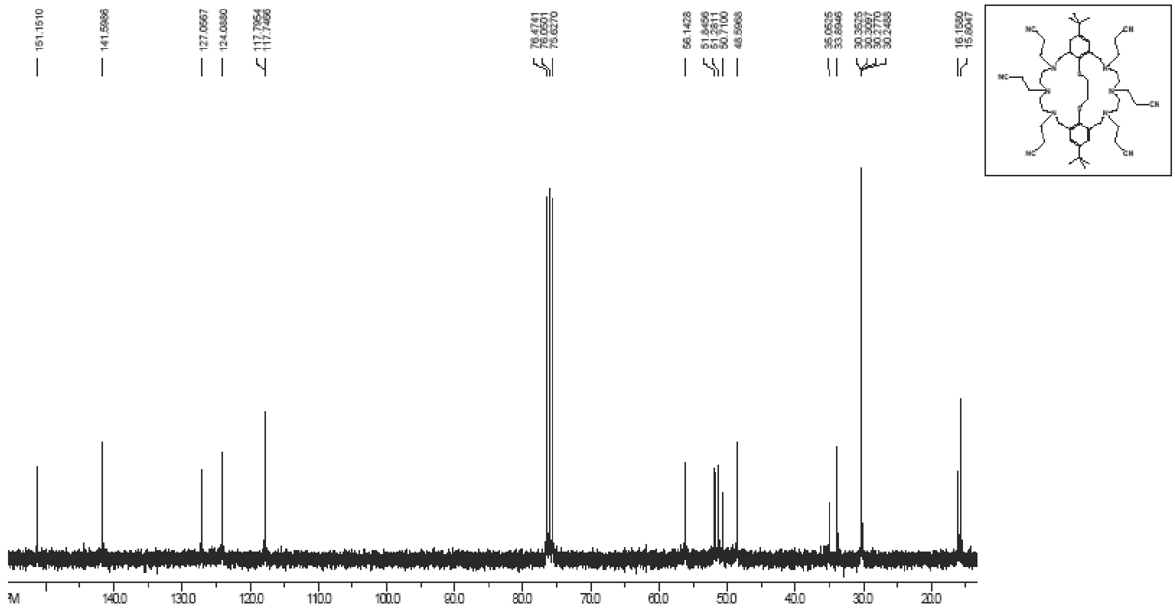


7. Spectra for hexa(cyanoethylated)aza-thioether **15**.

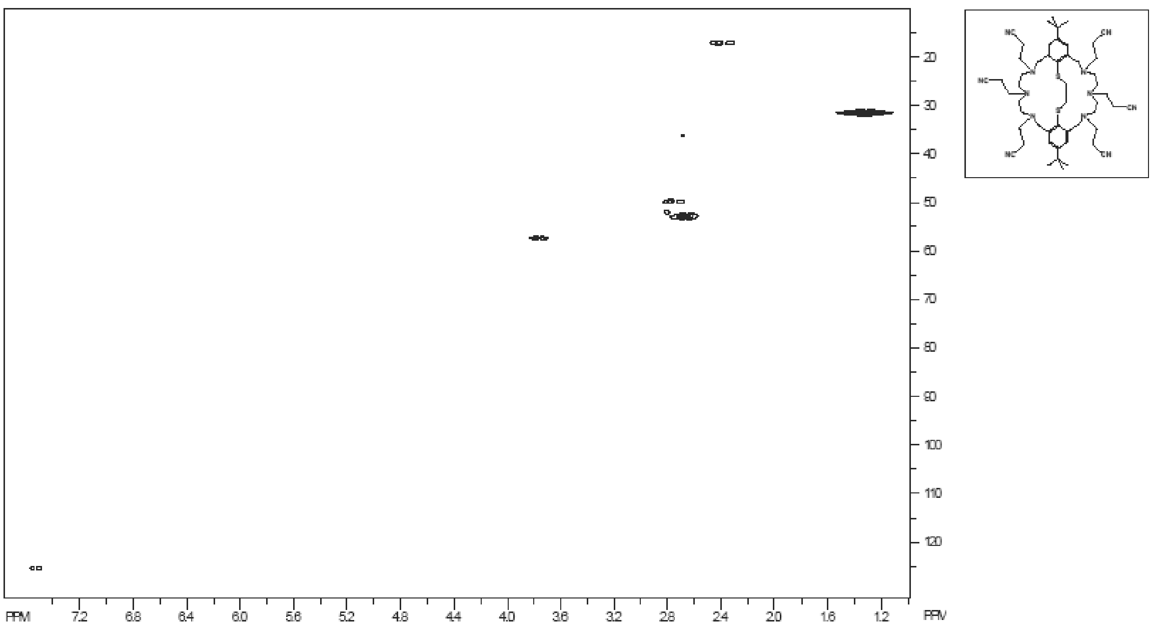


$^{1}H/^{1}H$-COSY

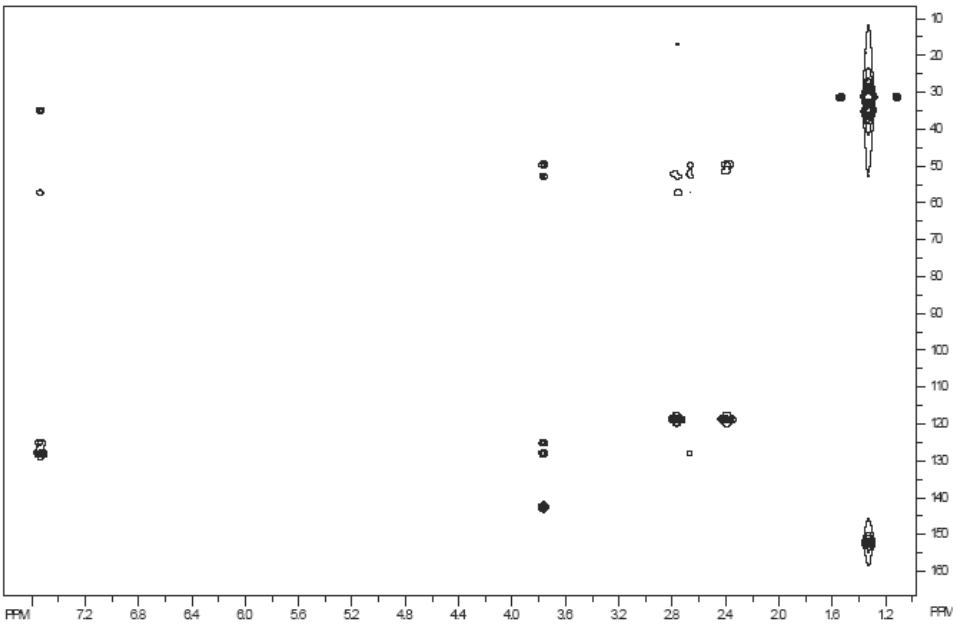


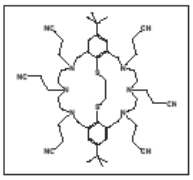

151.1510
141.5986
127.0567
124.0880
117.7954
117.7466
76.4741
76.0501
75.6270
56.1428
51.8456
51.2811
50.7100
48.5968
35.0525
33.8946
30.3525
30.3097
30.2770
30.2488
16.1580
15.8047
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0

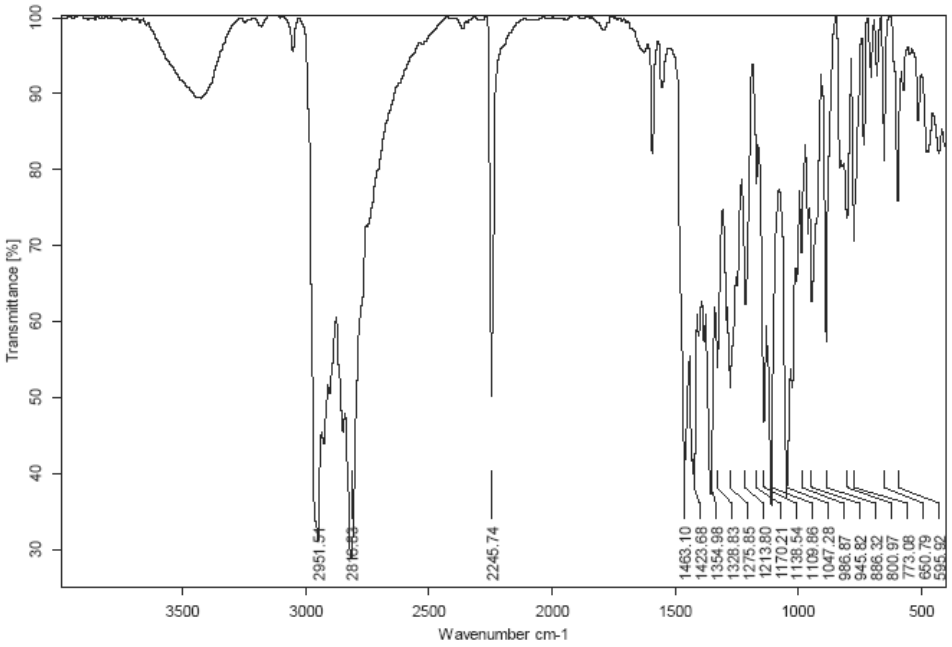
HSQC

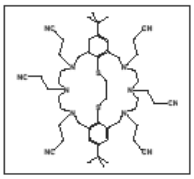

PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
20
30
40
50
60
70
80
90
100
110
120

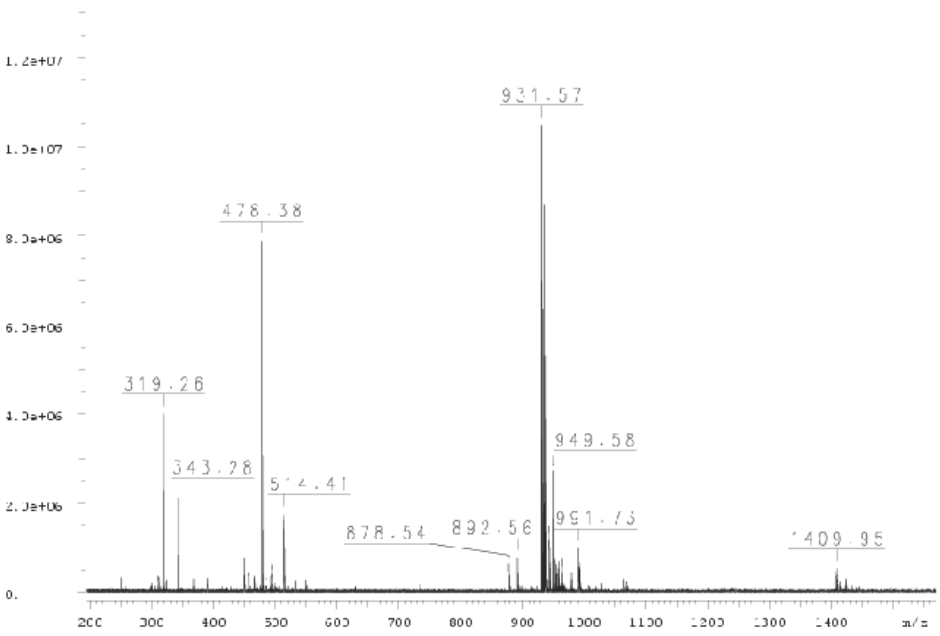
HMBC

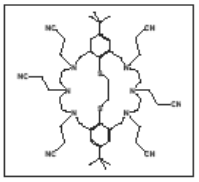

PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM



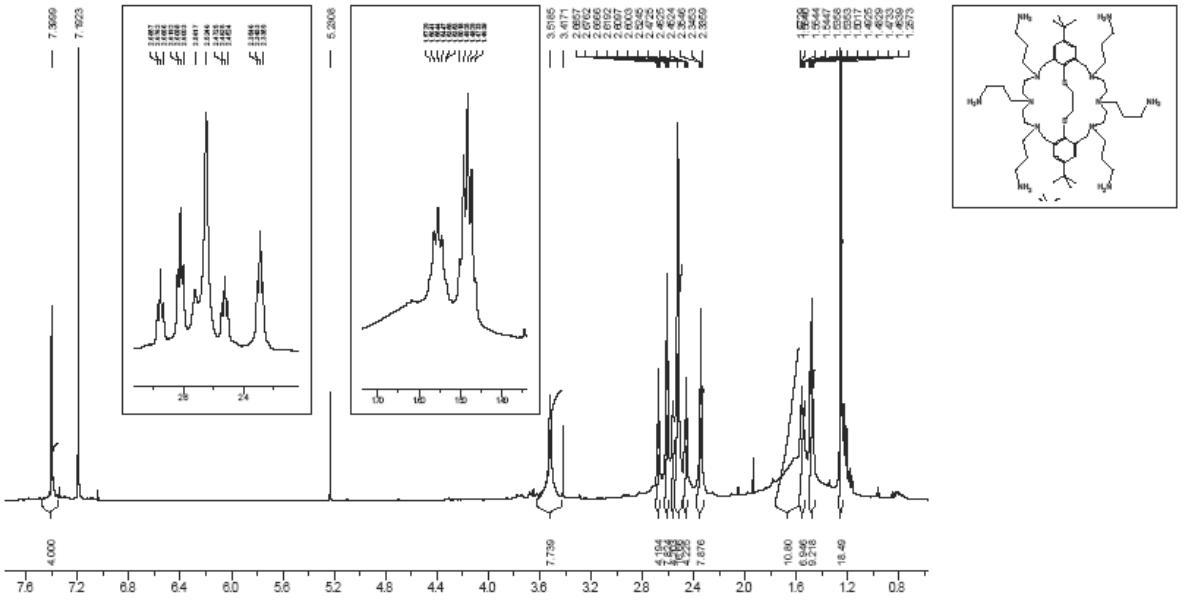

Transmittance [%]
Wavenumber cm-1
2951.54
2245.74
1463.10
1423.68
1354.98
1328.83
1275.85
1213.80
1170.21
1138.54
1109.86
1047.28
986.87
945.82
886.32
800.97
773.08
650.79
595.92



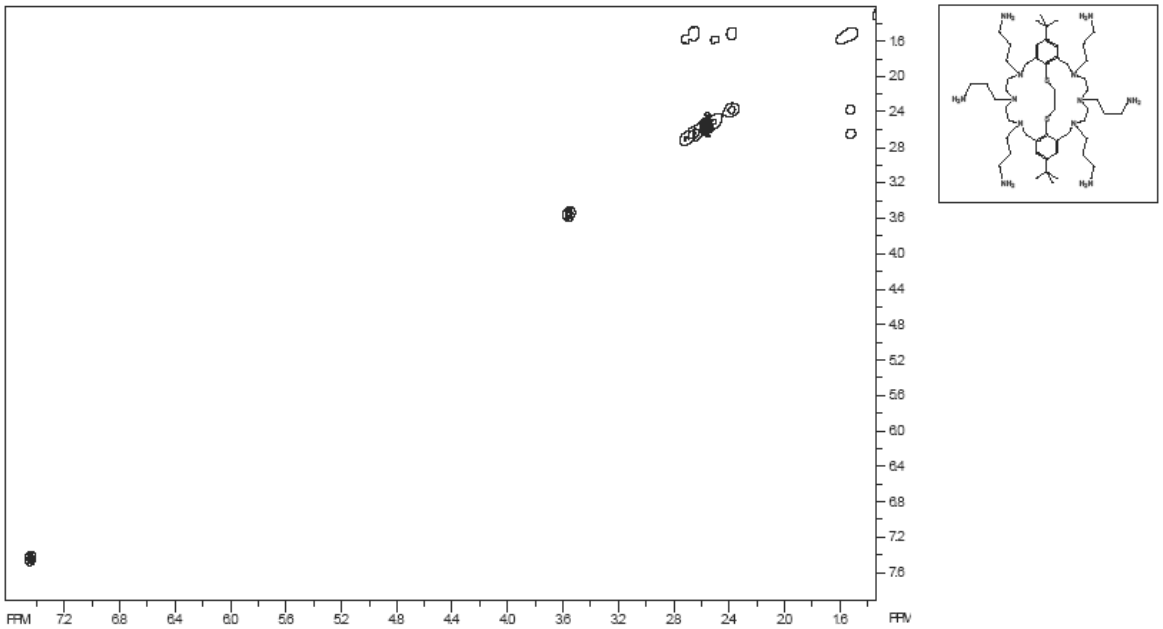

931.57
478.38
319.26
343.28
949.58
878.54
892.56
951.73
1409.95
m/z

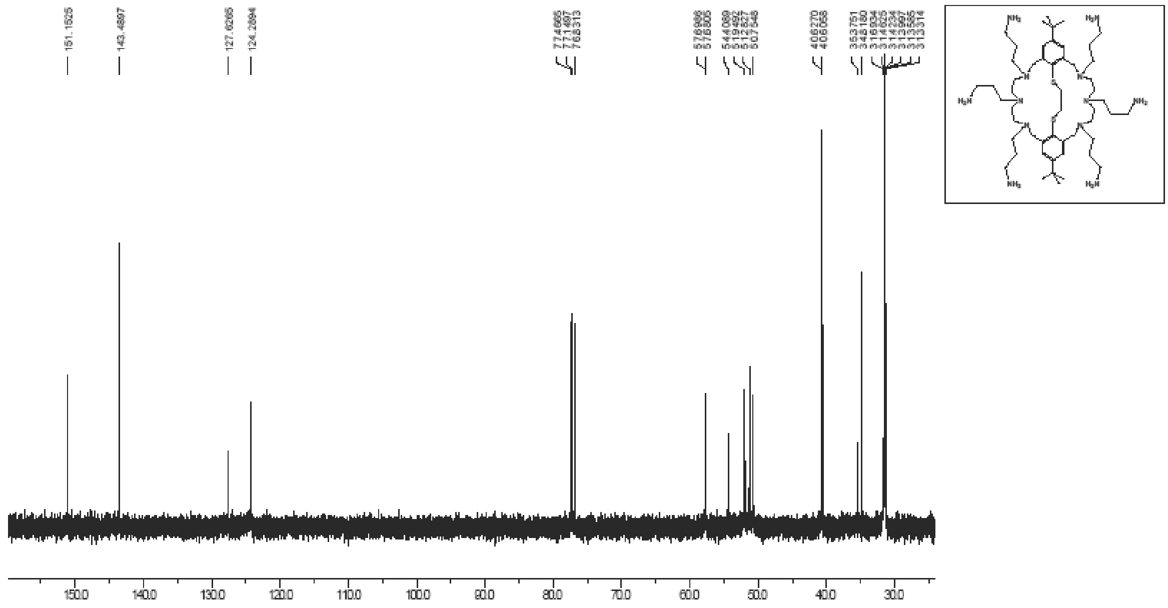


8. Spectra for hexa(3-aminopropylated)aza-thioether **16**.

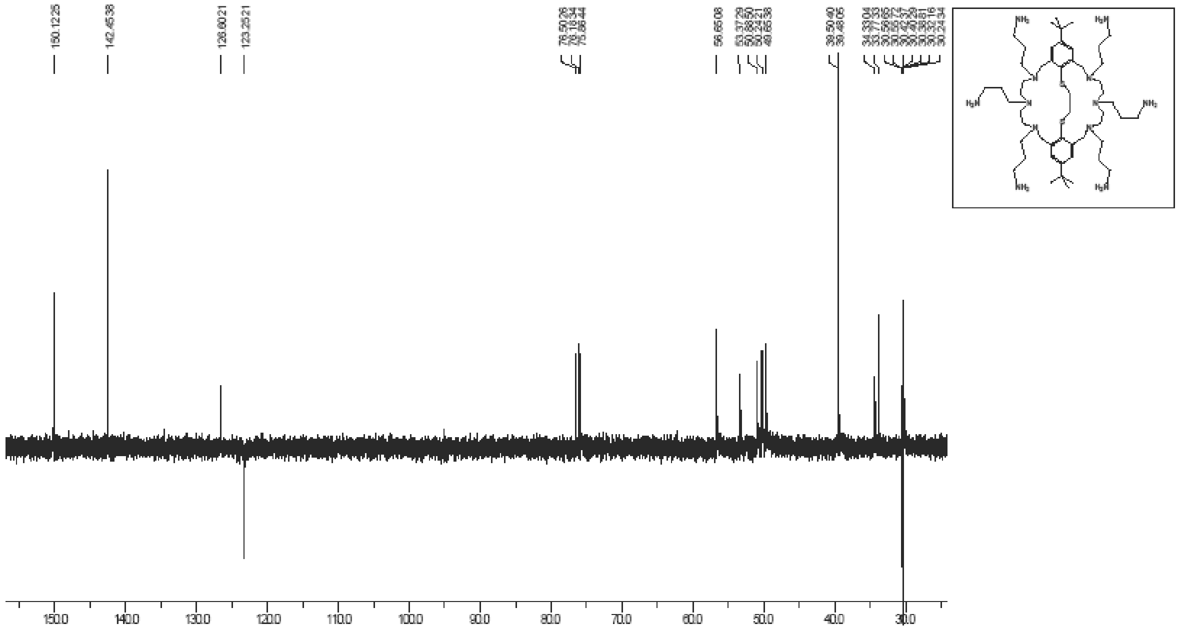


$^{1}H/^{1}H$-COSY

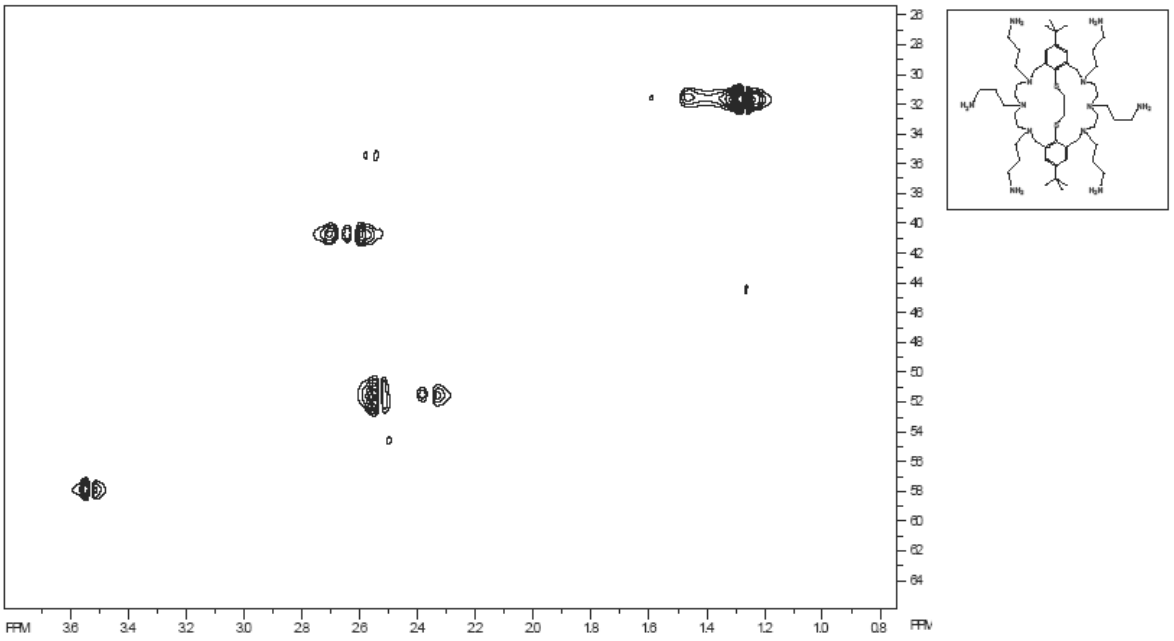



150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0

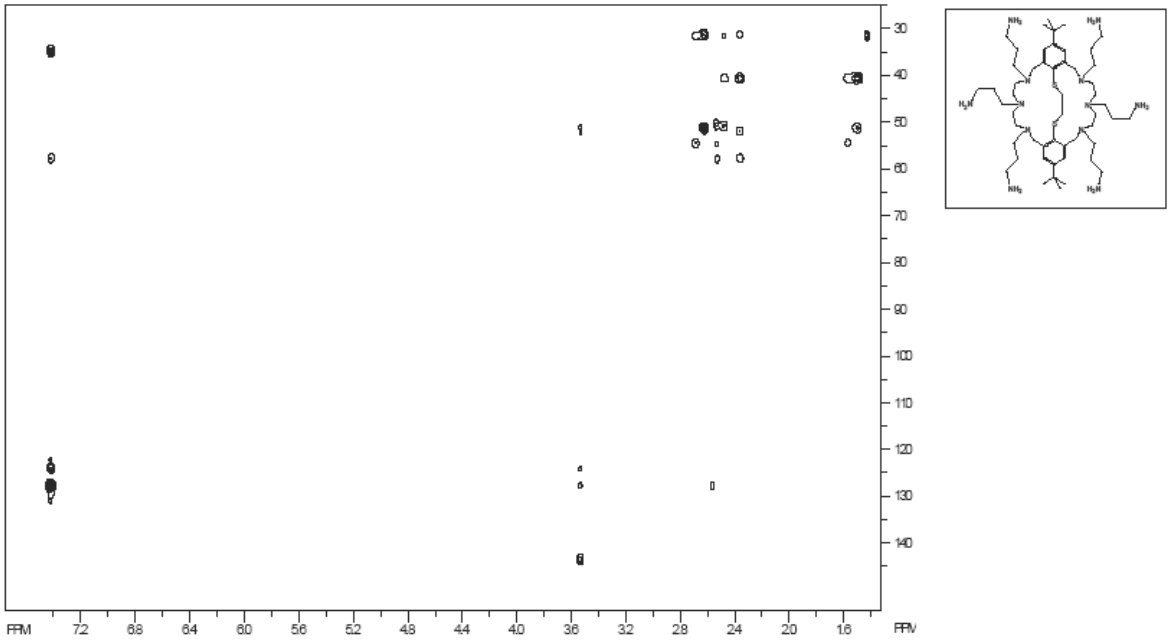
APT


150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0

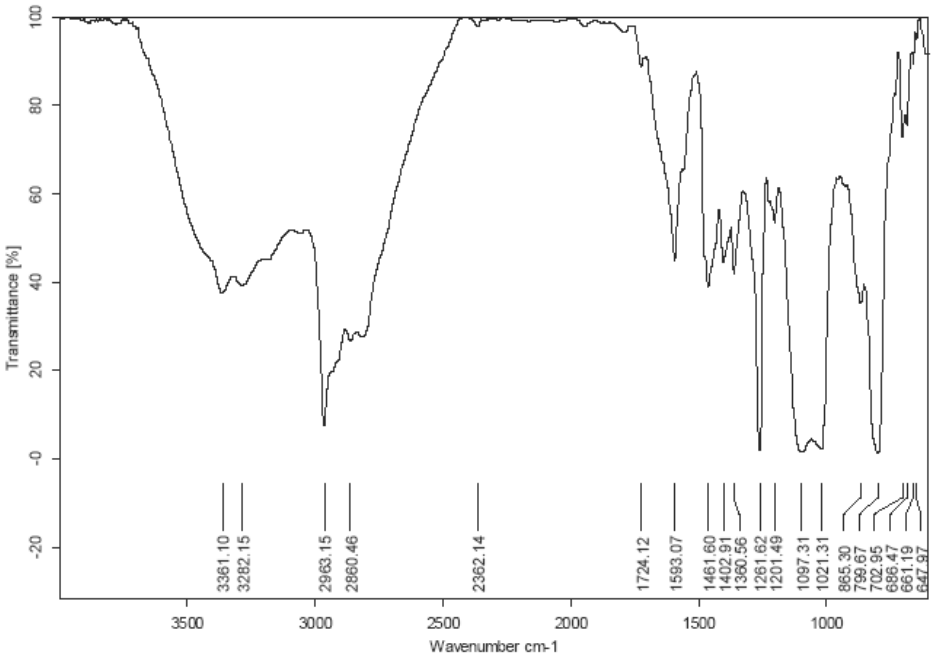
HSQC

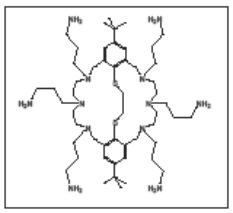

PPM
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
PPM

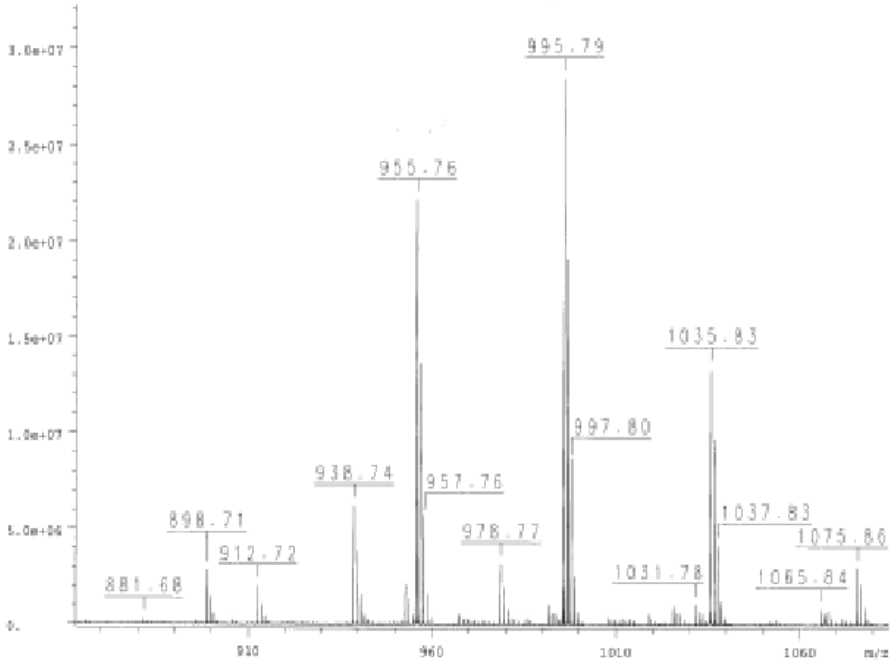
HMBC

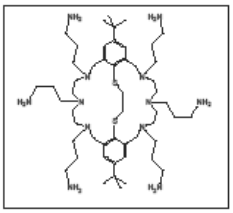

PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
PPM

IR- Spektrum

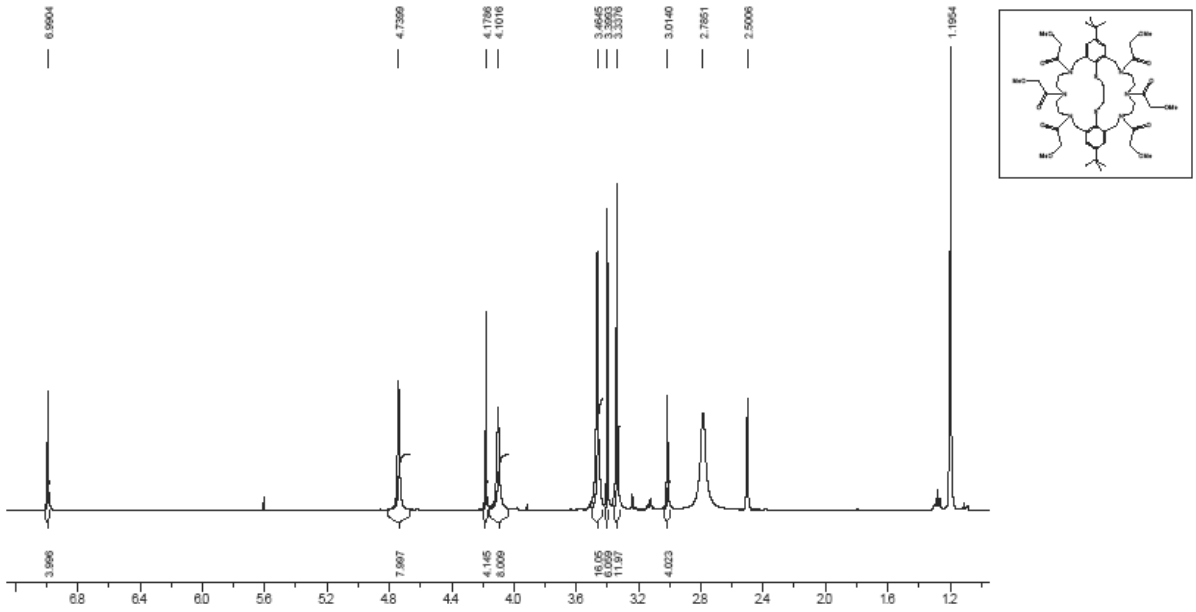

Transmittance [%]
100
80
60
40
20
-0
-20
3361.10
3282.15
2963.15
2860.46
2362.14
1724.12
1593.07
1461.60
1402.91
1360.56
1261.62
1201.49
1097.31
1021.31
865.30
799.67
702.95
686.47
661.19
647.97
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

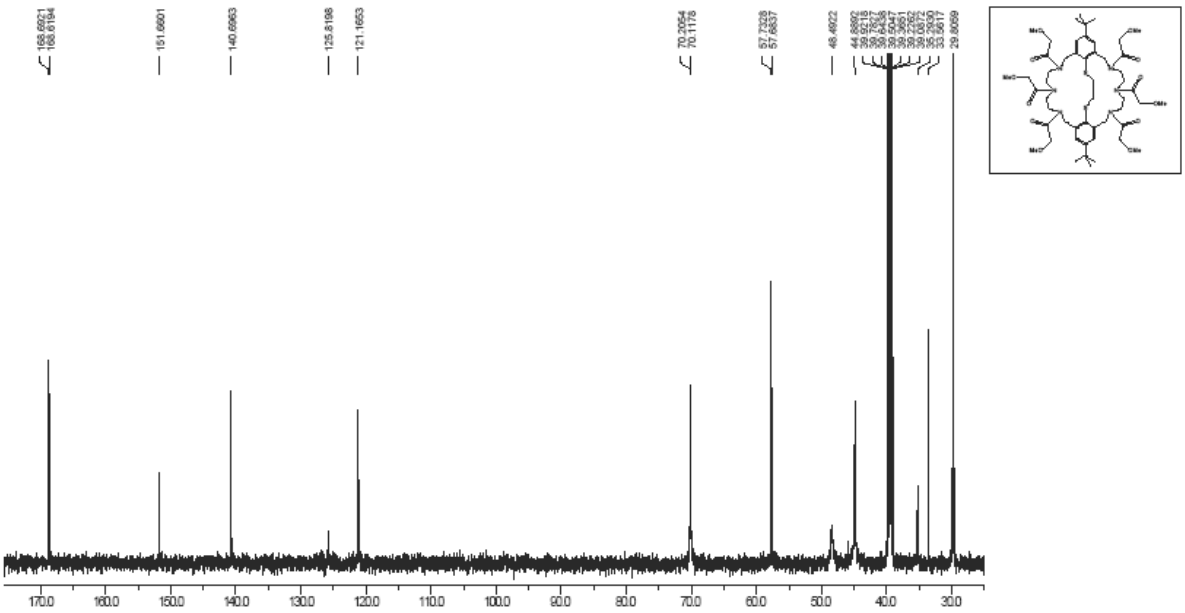



995.79
955.76
1035.83
997.80
938.74
957.76
1037.83
898.71
978.77
1075.86
912.72
1031.78
1065.84
881.68
910
960
1010
1060
m/z

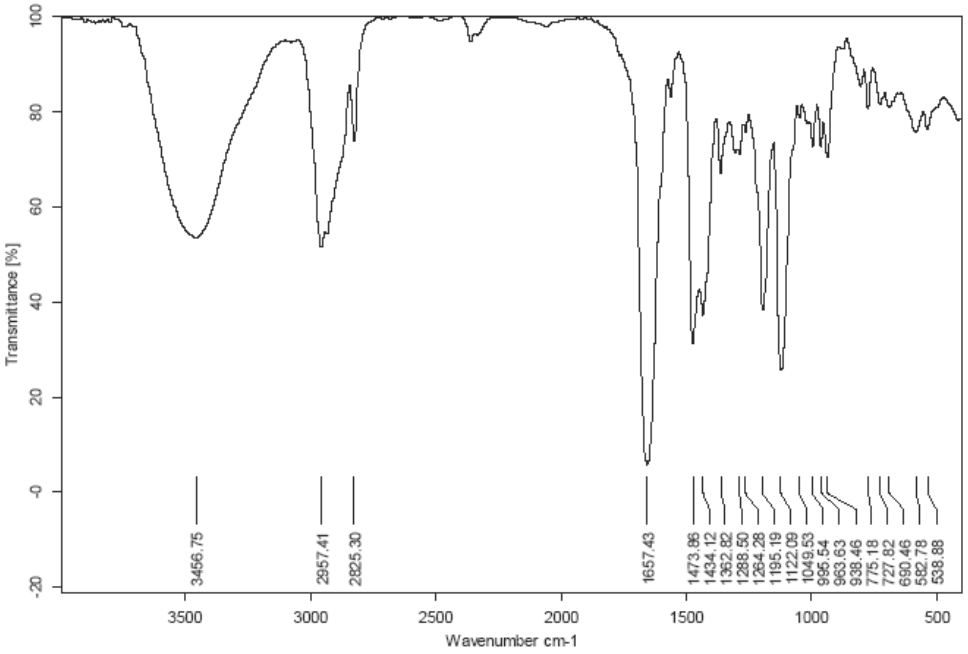


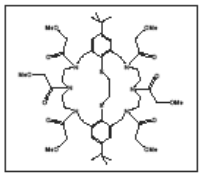
9. Spectra for hexa(2-methoxyacetylated)aza-thioether **17**.

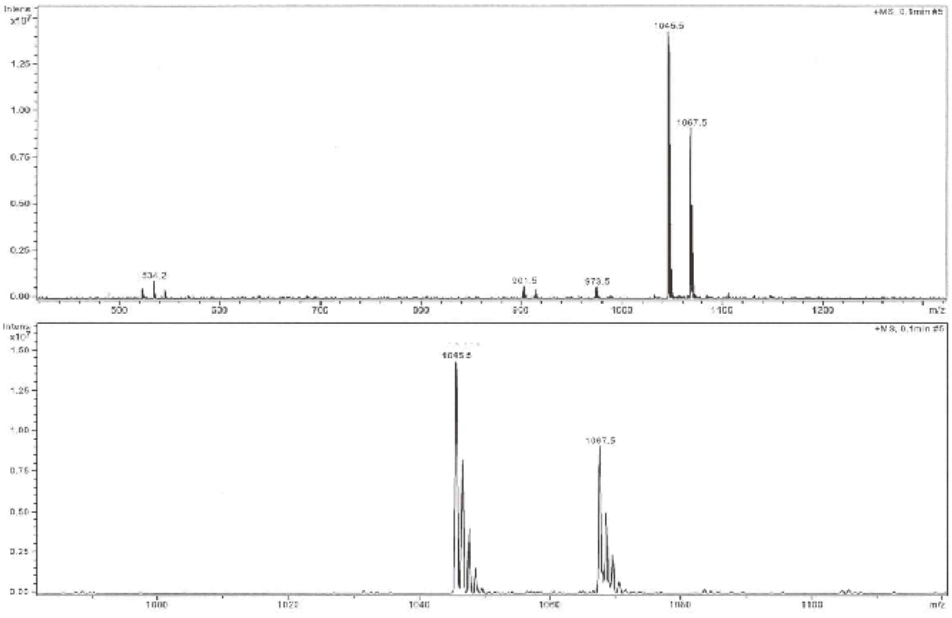


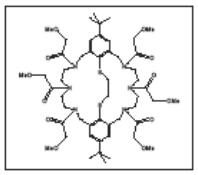


IR-Spektrum


Transmittance [%]
100
80
60
40
20
-0
-20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3456.75
2957.41
2825.30
1657.43
1473.86
1434.12
1362.82
1288.50
1264.28
1195.19
1122.09
1049.53
995.54
963.63
938.46
775.18
727.92
690.46
582.78
538.88

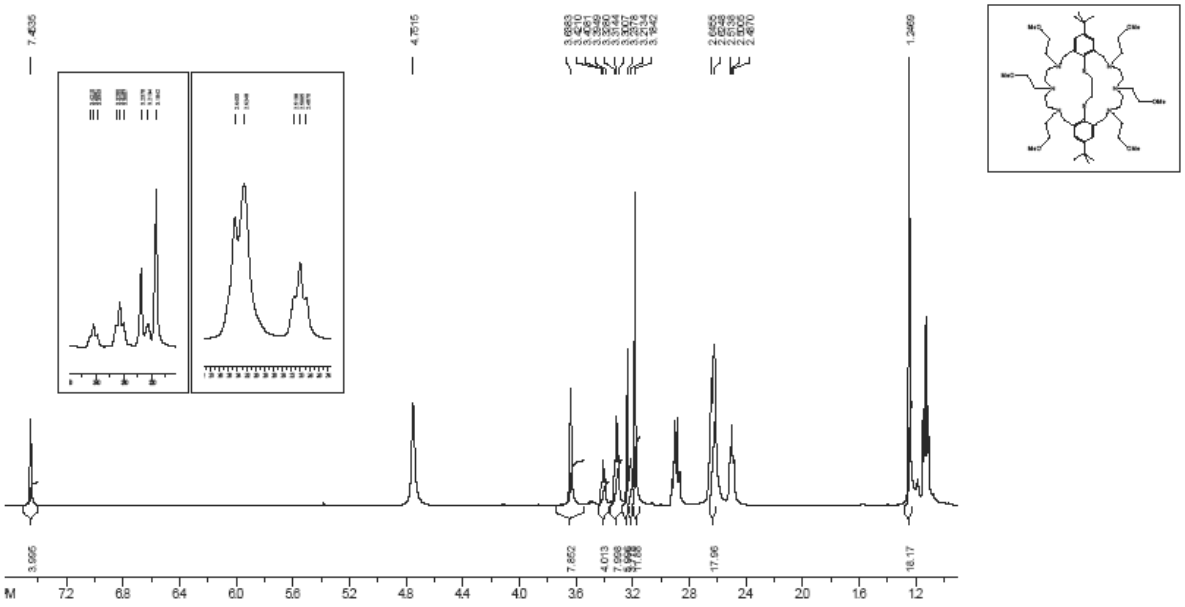



1045.5
1067.5
534.2
921.5
973.5
m/z
1045.5
1067.5
m/z

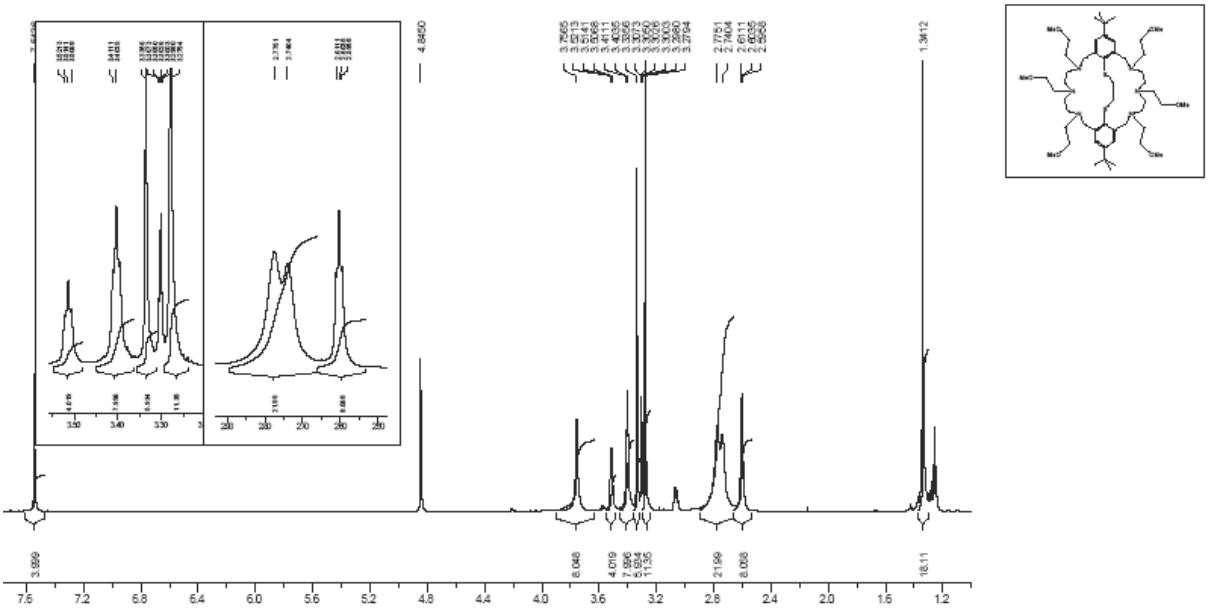


10. Spectra for hexa(2-methoxyethylated)aza-thioether **18**.

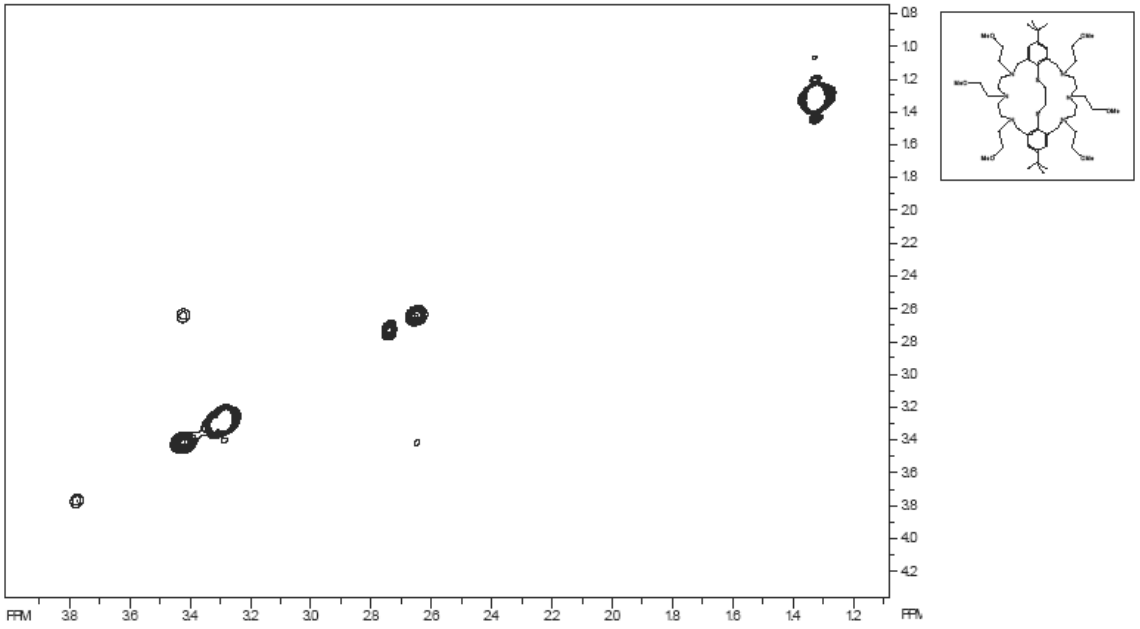
^{1}H NMR (400 MHz, $CDCl_3$)

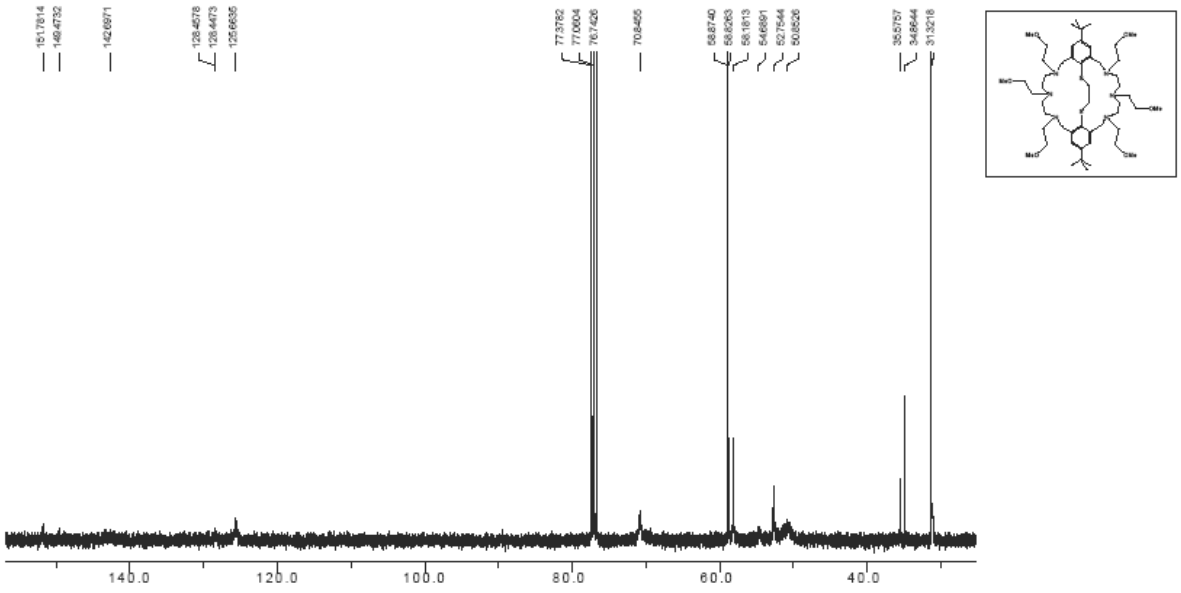


1H NMR (700 MHz, CD_3OD)

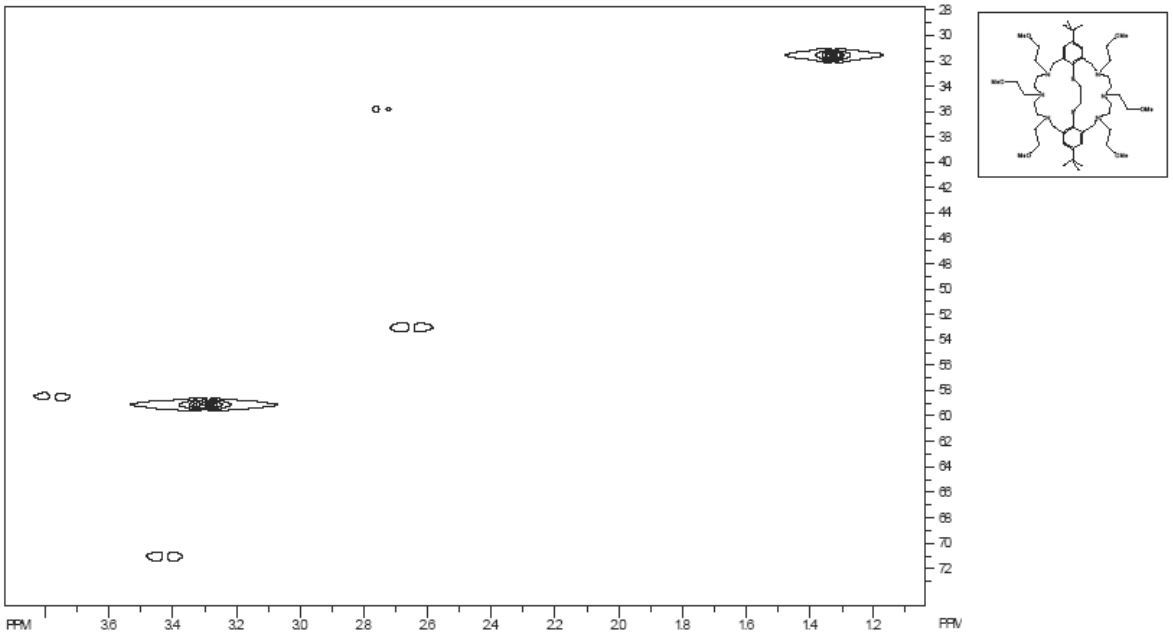


$^{1}H/^{1}H$-COSY

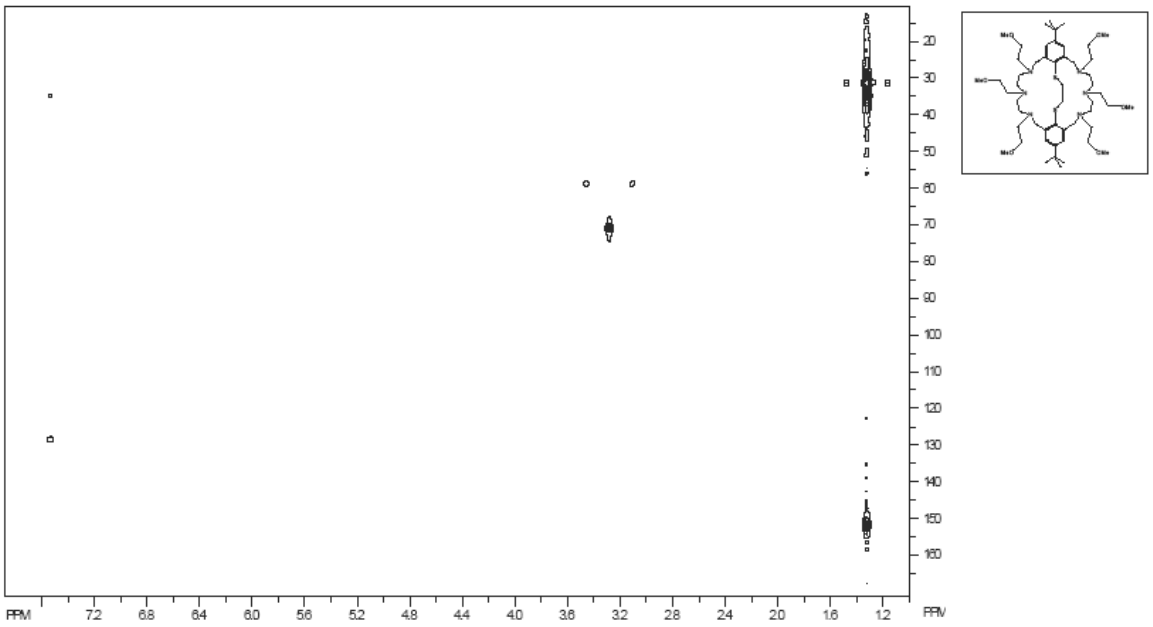

0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
PPM
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
PPM


151.7614
149.4732
142.6971
128.4578
128.4473
125.6635
77.3782
77.0604
76.7426
70.8455
58.8740
58.8263
58.1613
54.6881
52.7544
50.8526
35.5757
34.8644
31.3216
140.0
120.0
100.0
80.0
60.0
40.0

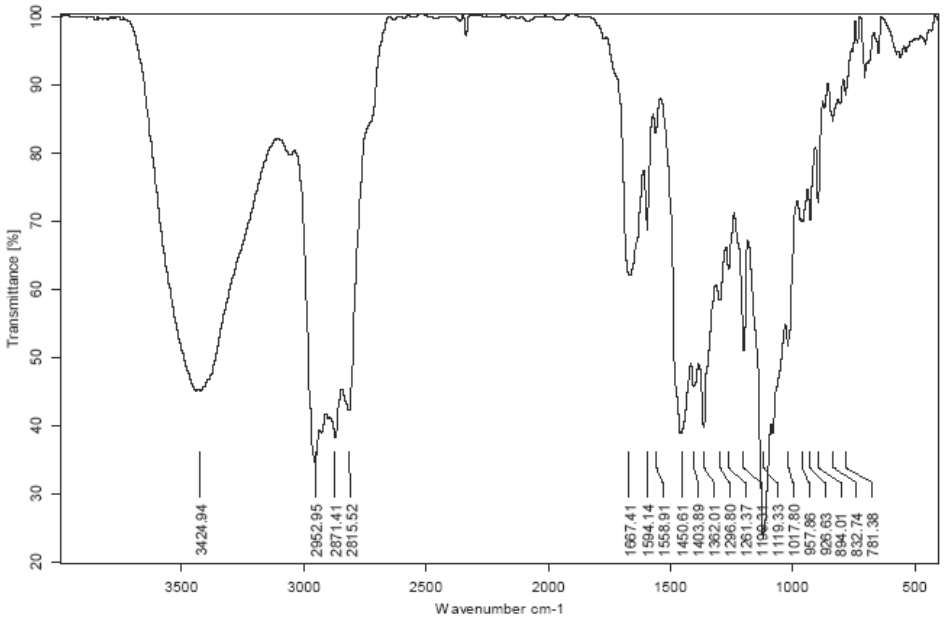
HSQC

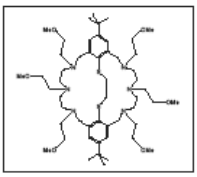

28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
PPM
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
PPM

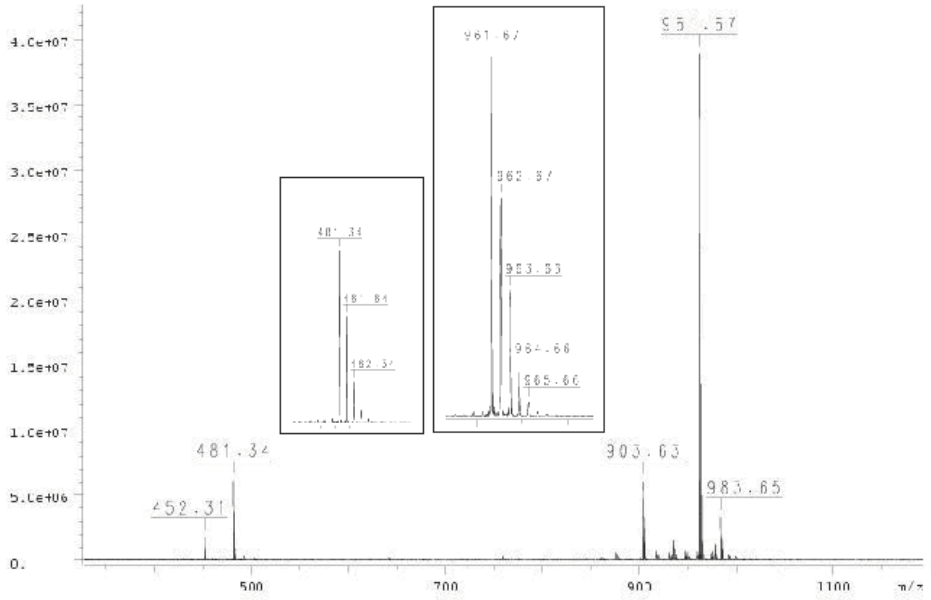
HMBC

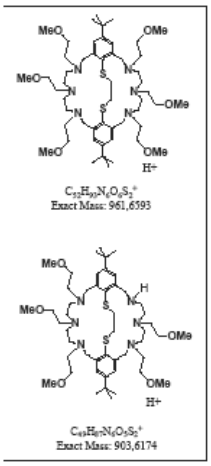

20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM

IR-Spektrum

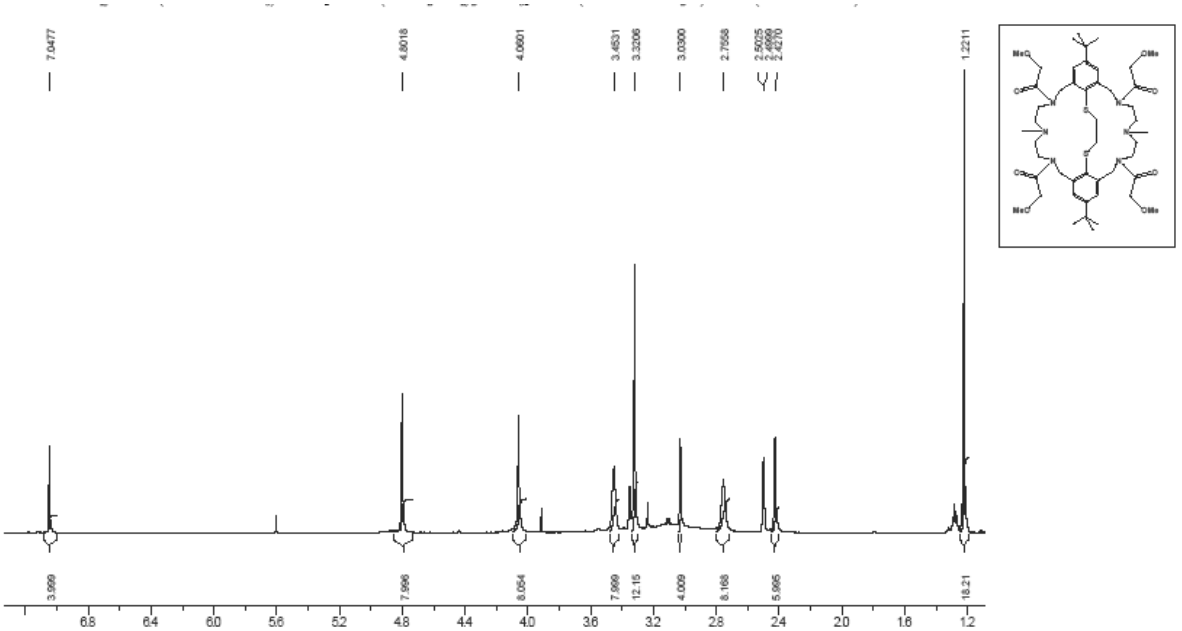

Transmittance [%]
Wavenumber cm-1
3424.94
2952.95
2871.41
2815.52
1667.41
1594.14
1558.91
1450.61
1403.89
1362.01
1296.80
1261.37
1119.33
1017.80
957.88
926.63
894.01
832.74
781.38

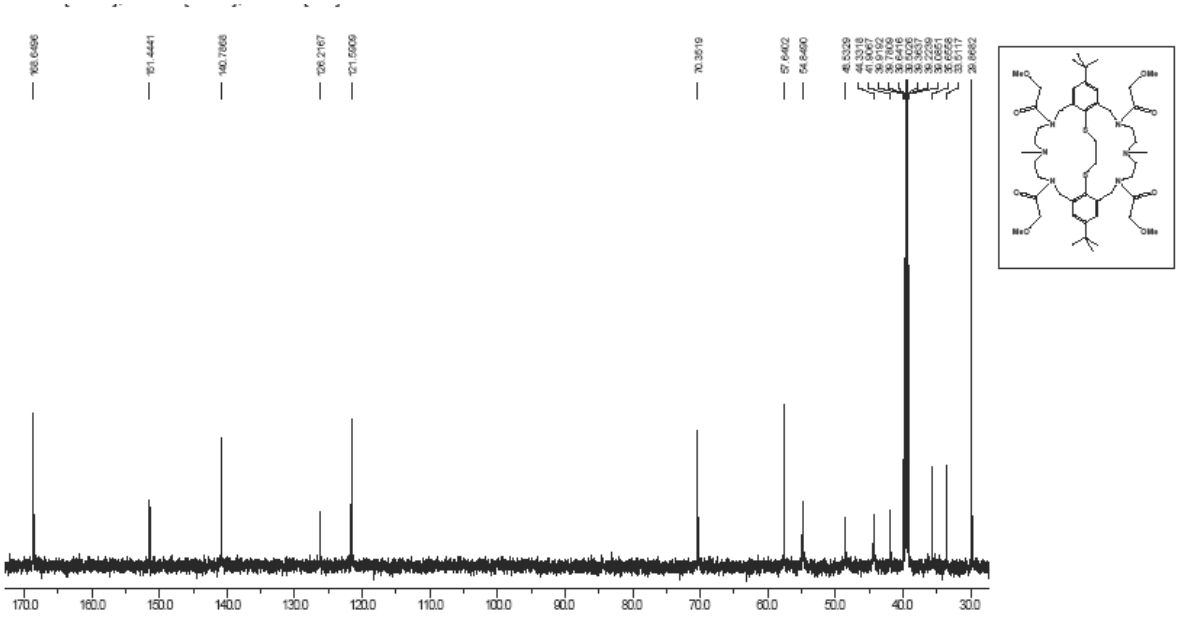



481.34
452.31
903.63
983.65
961.67
962.67
963.53
964.66
965.66

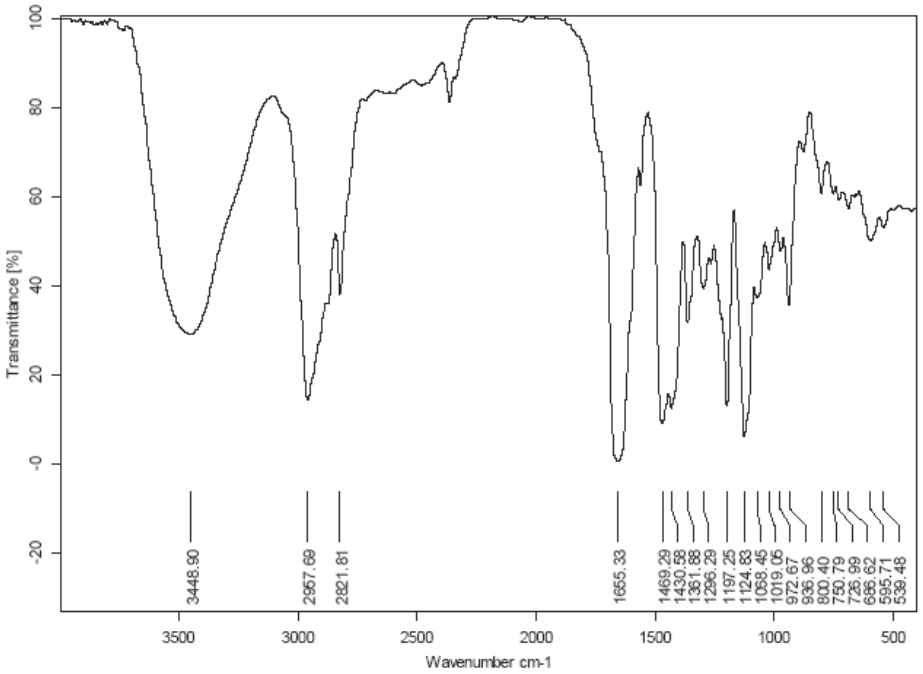

MeO
OMe
H+
C72H92N6O8S2+
Exact Mass: 961,6593
C48H60N6O8S2+
Exact Mass: 903,6174

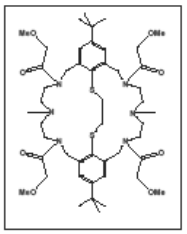
11. Spectra for tetra(2-methoxyacetylated)aza-thioether **19**.

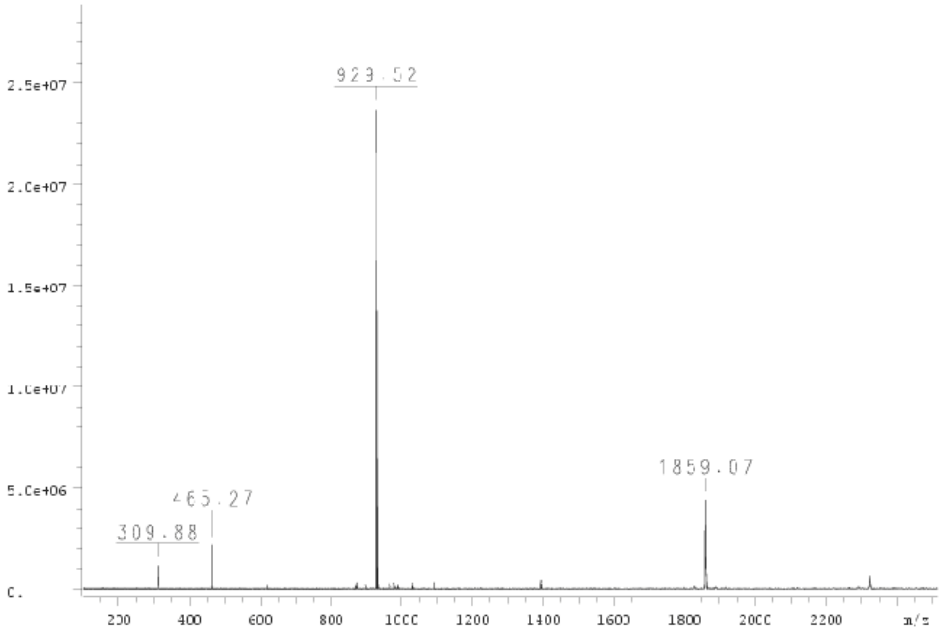


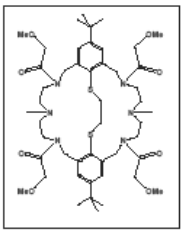


IR- Spektrum

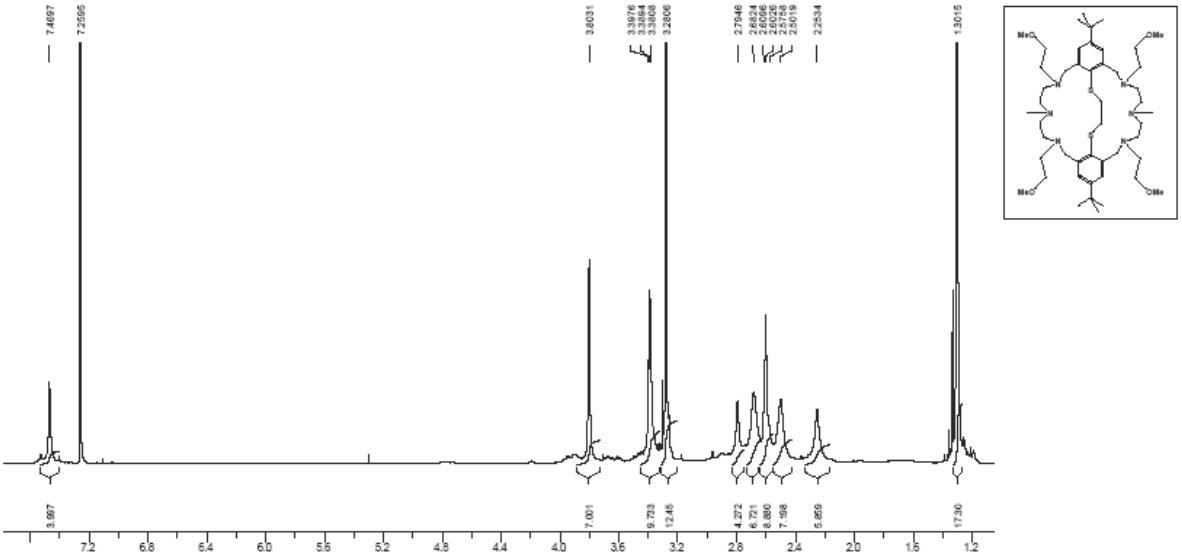

Transmittance [%]
100
80
60
40
20
-0
-20
3448.90
2957.69
2821.81
1655.33
1469.29
1430.58
1381.88
1296.29
1197.25
1124.83
1058.45
1019.05
972.67
936.96
800.40
750.79
726.99
686.62
595.71
539.48
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



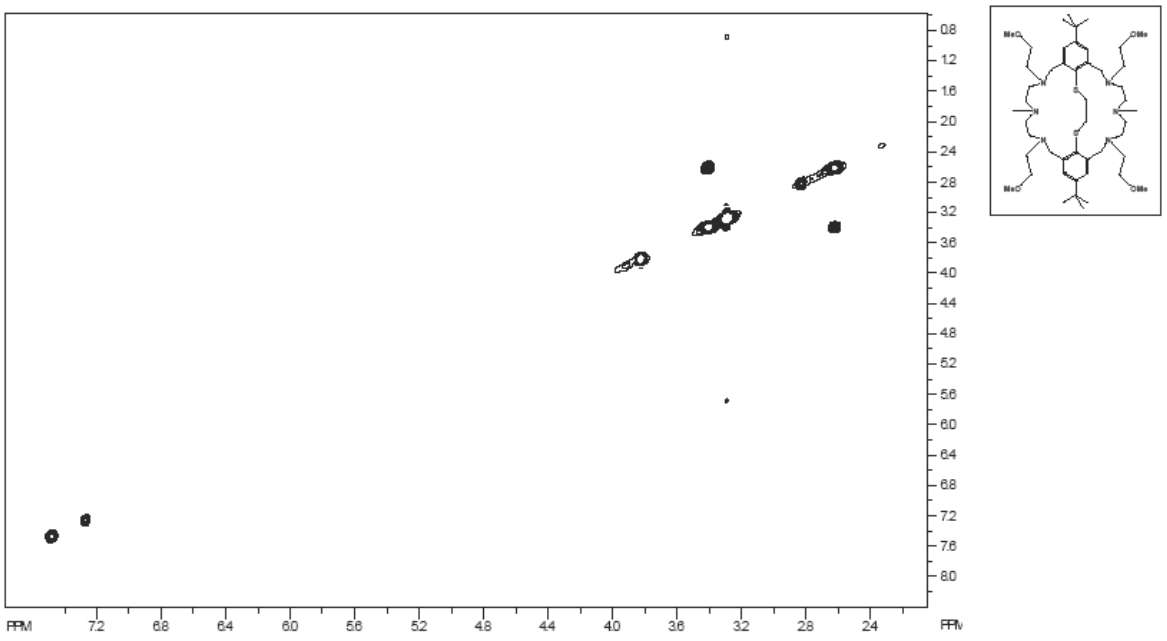

2.5e+07
2.0e+07
1.5e+07
1.0e+07
5.0e+06
0.
923.52
1859.07
465.27
309.88
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
m/z

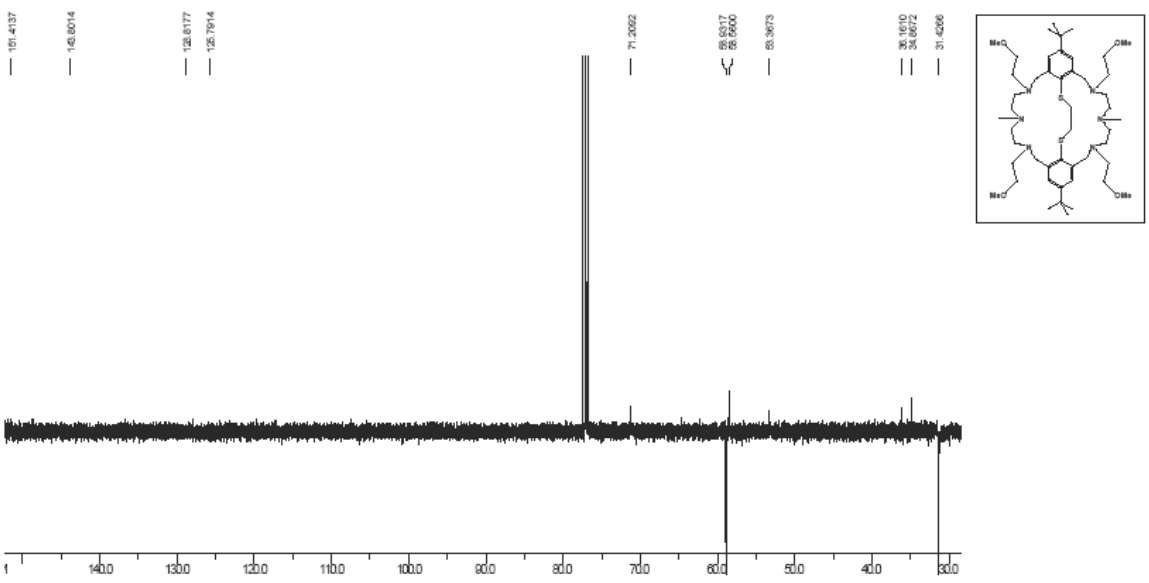


12. Spectra for tetra(2-methoxyethylated)aza-thioether **20**.

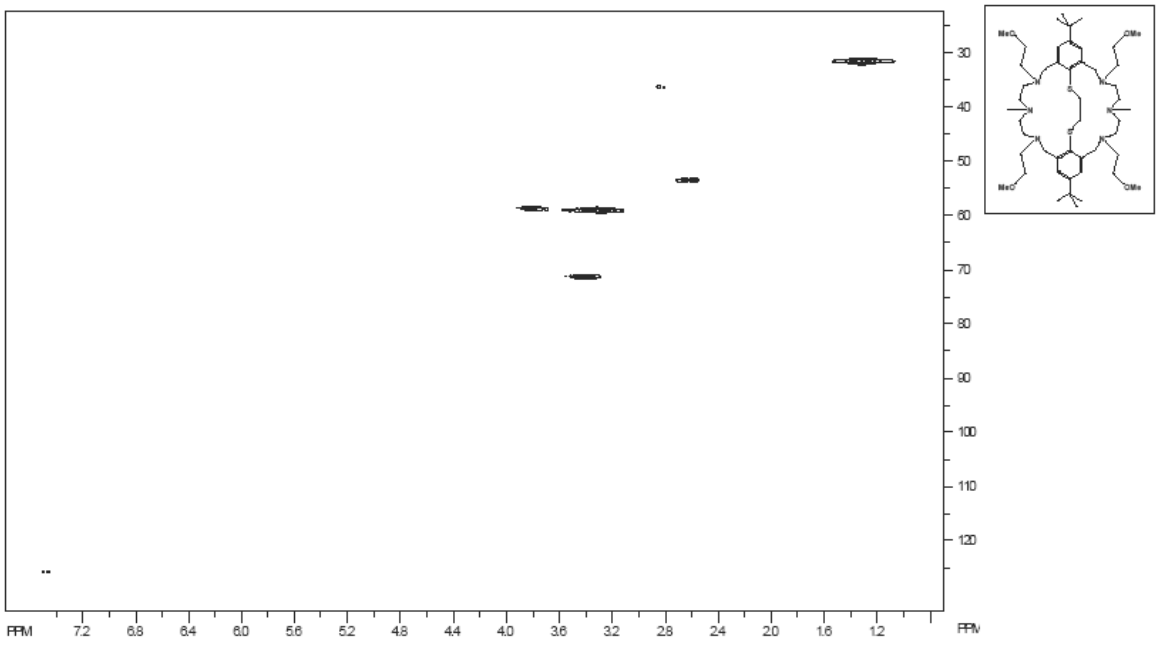


$^1H/^1H$- COSY

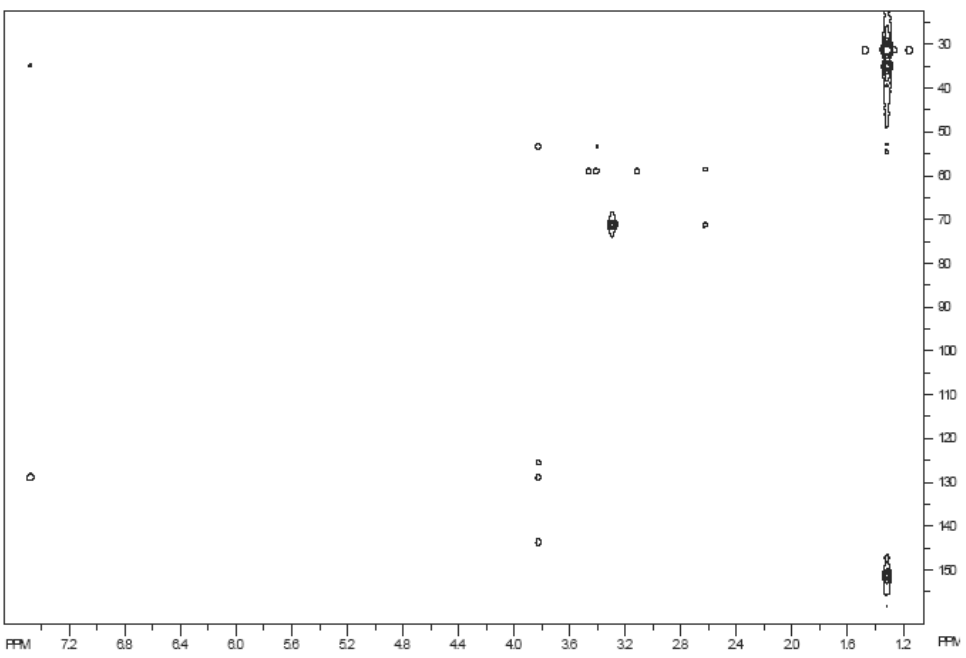


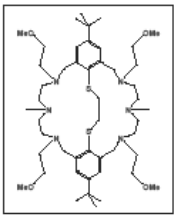

151.4137
143.6014
128.6177
125.7914
71.2092
69.6217
69.5600
55.3673
36.1610
34.6672
31.4266
MeO
OMe
MeO
OMe
1
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0

HSQC

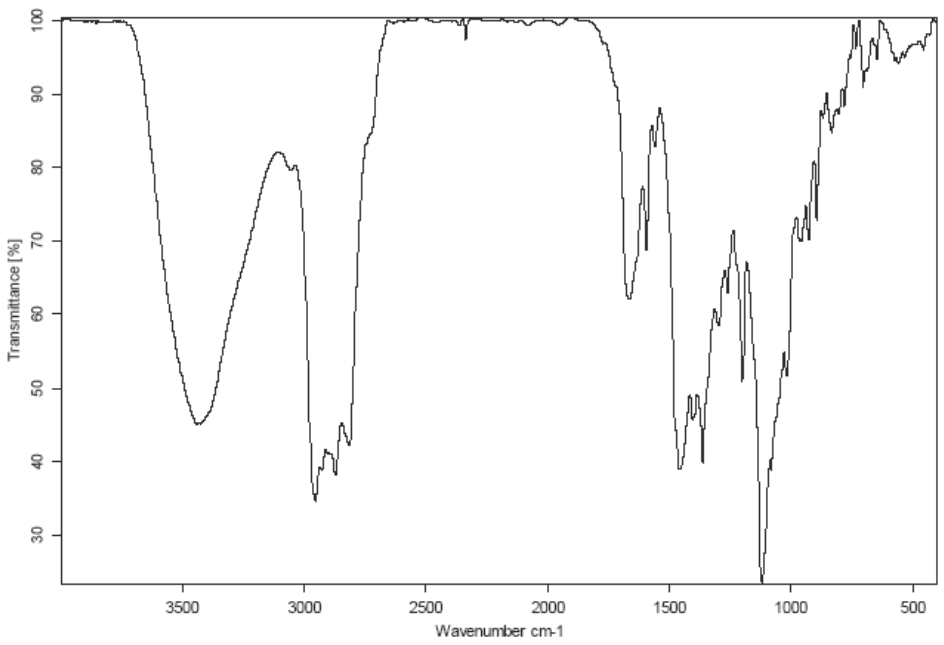

MeO
OMe
MeO
OMe
30
40
50
60
70
80
90
100
110
120
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM

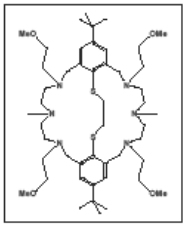
HMBC

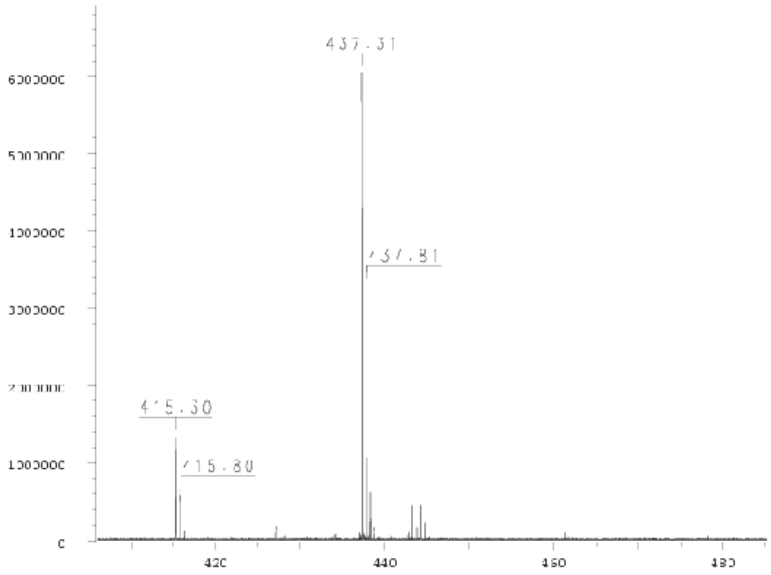




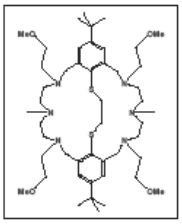
IR- Spektrum



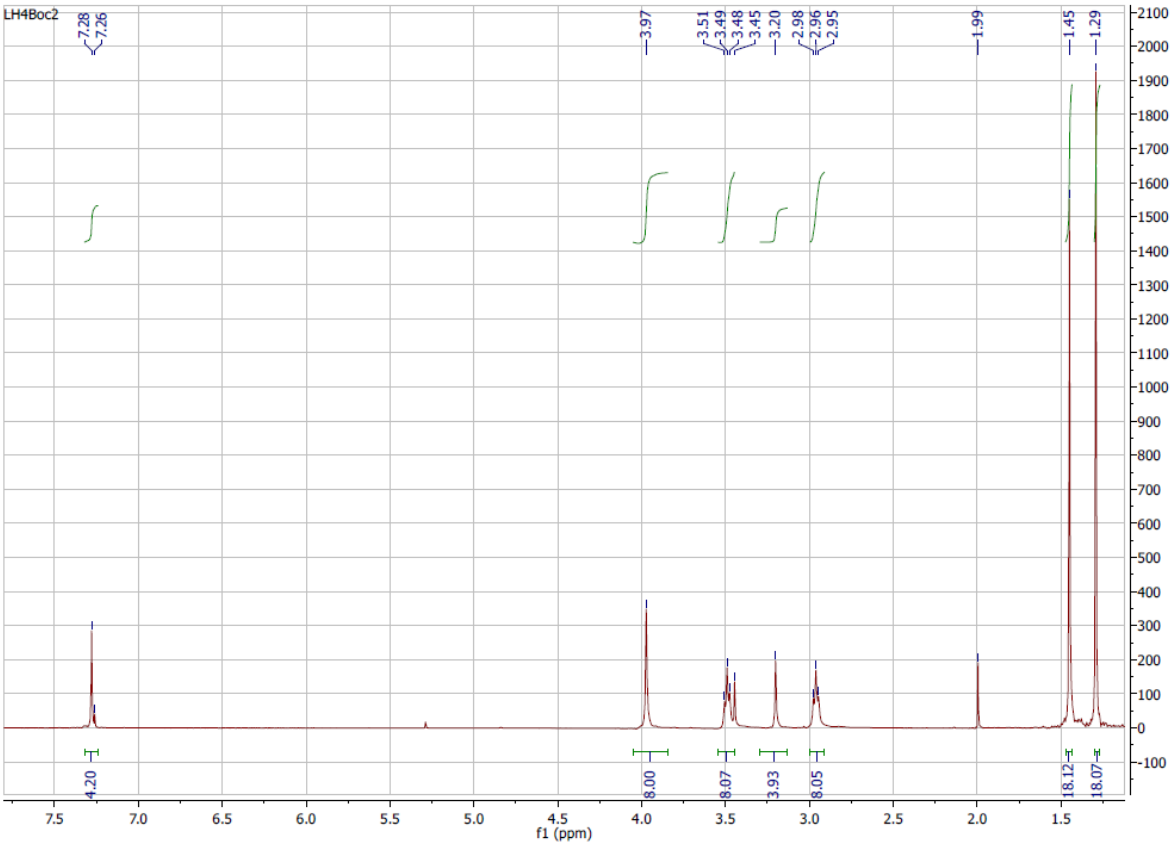


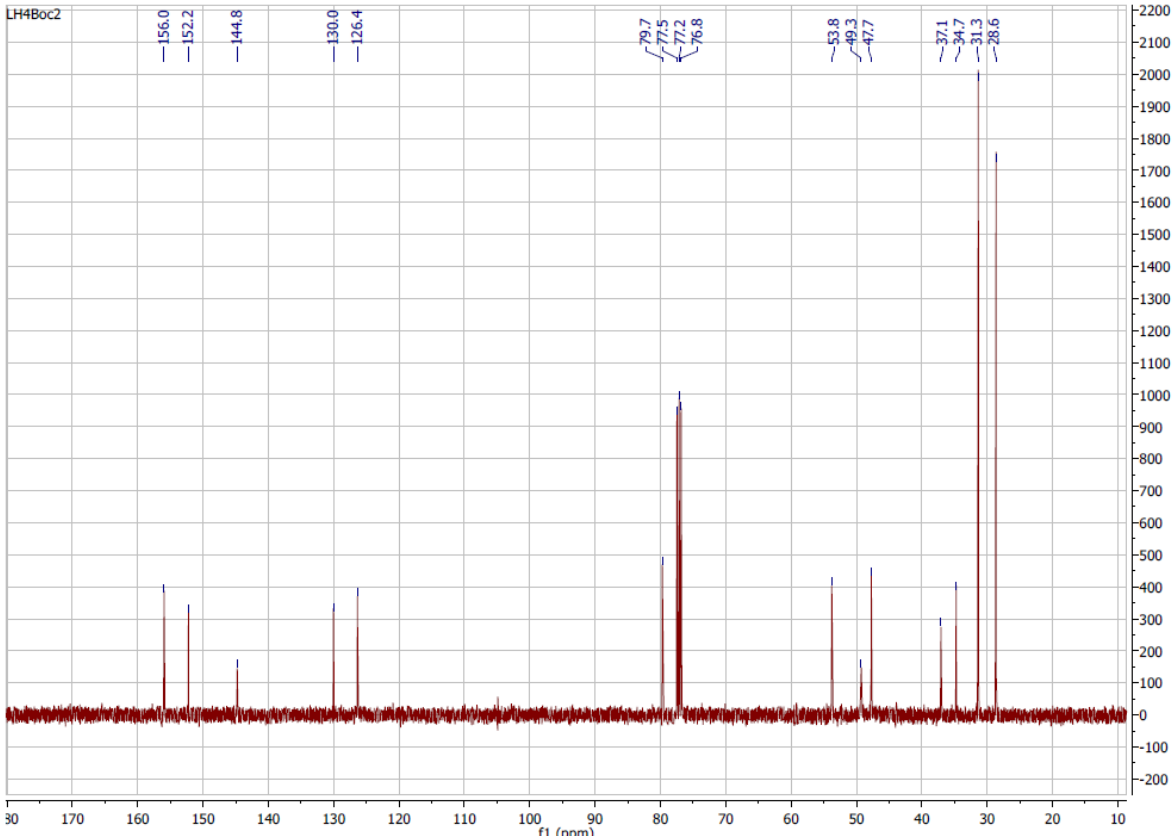

437.31
437.81
415.30
415.80
6000000
5000000
4000000
3000000
2000000
1000000
0
420
440
460
480

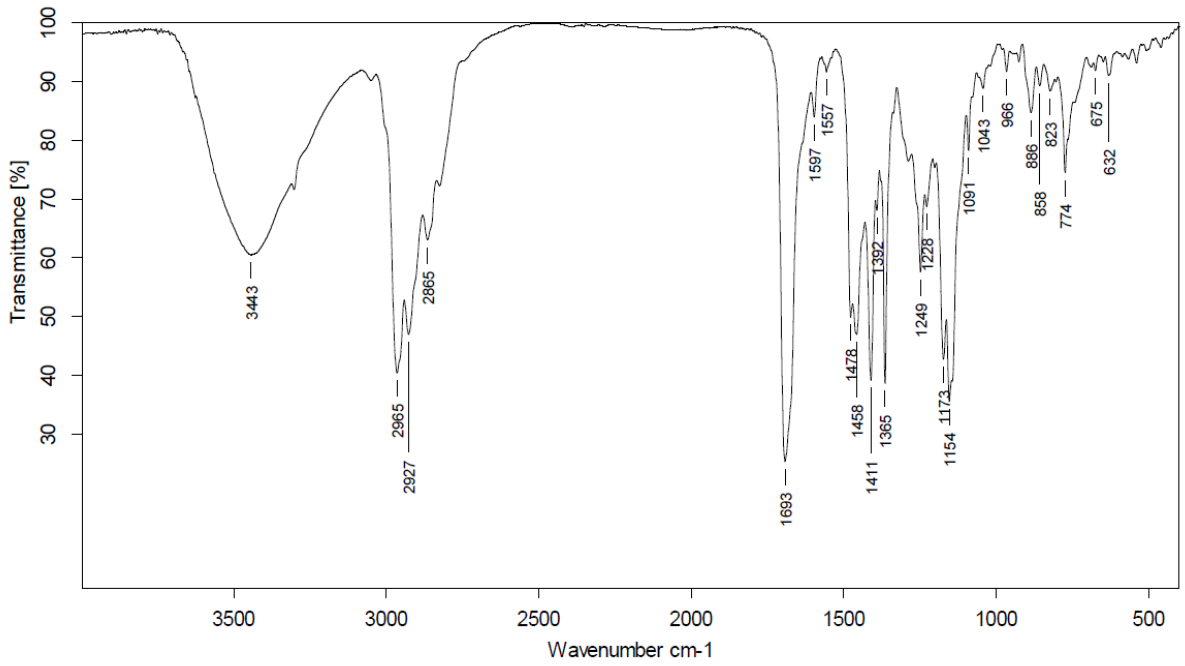

873.61
870



13. Spectra for dicarbamolyated macrobicycle **22**.



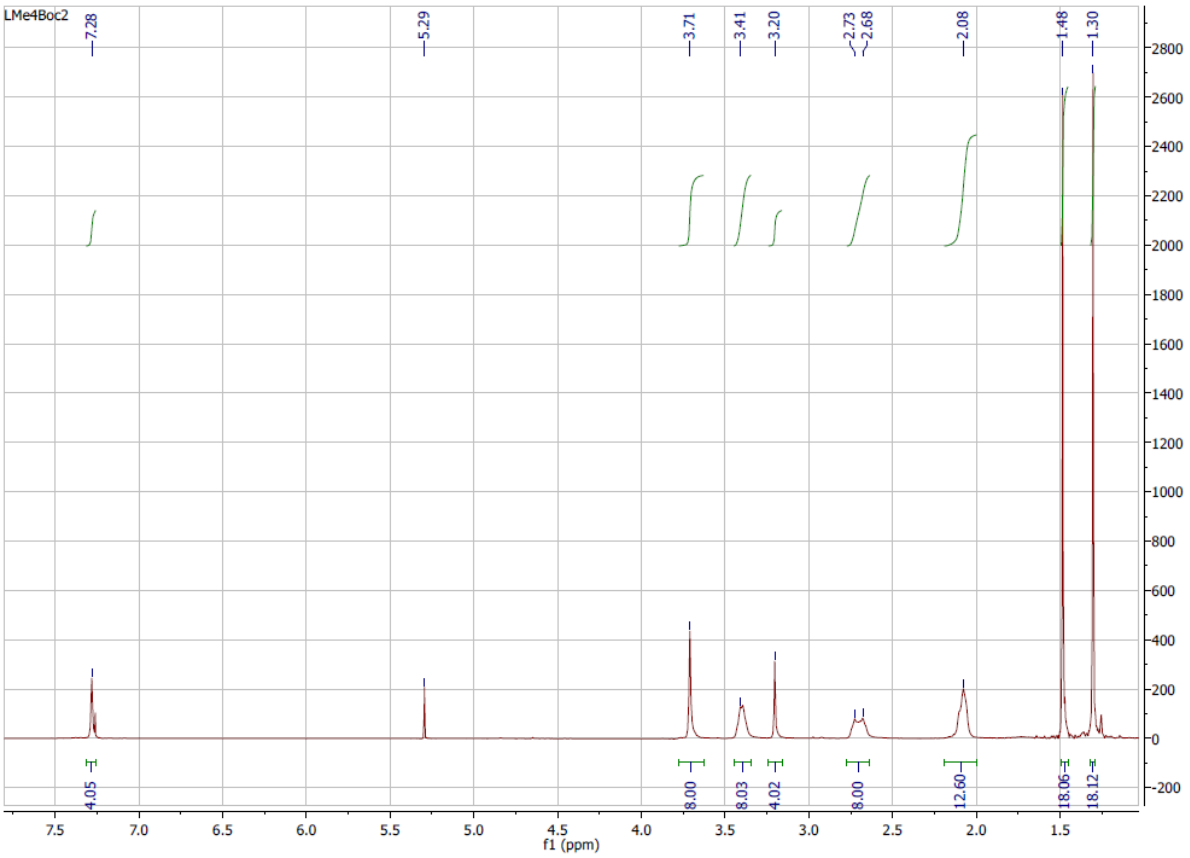


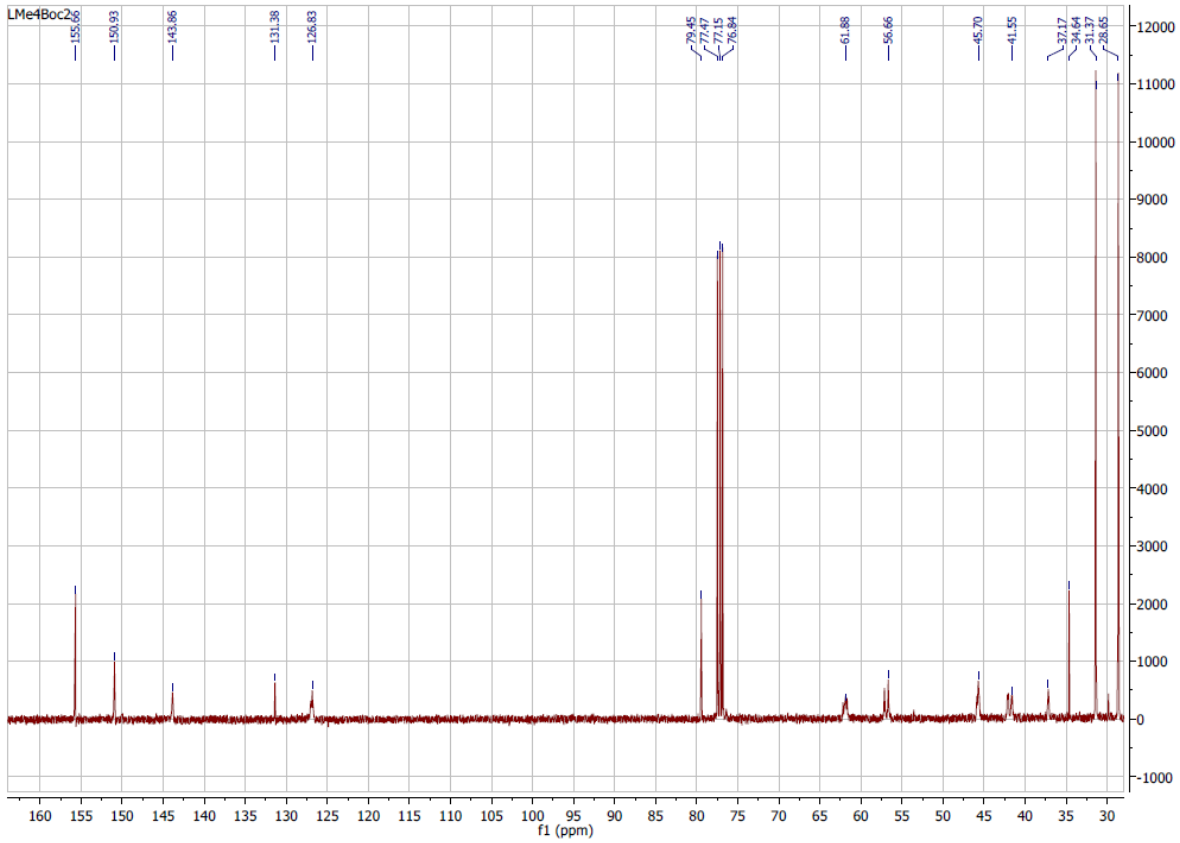


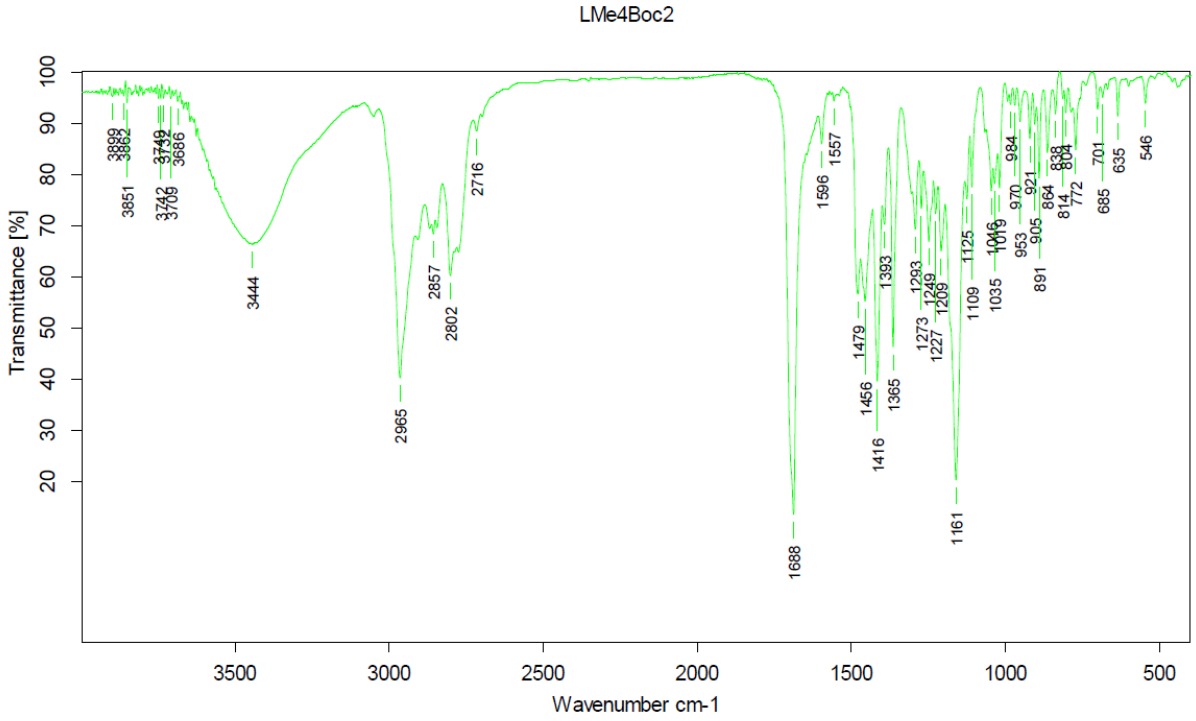
Messxperiment: Standard.XPM

Pfad: C:\IR\Kersting\Uli\BocLigand

14. Spectra for methylated macrobicycle **23**.







Messxperiment: Standard.XPM

Pfad: C:\IR\Kersting\Uli\BocLigand\LMe4Boc2

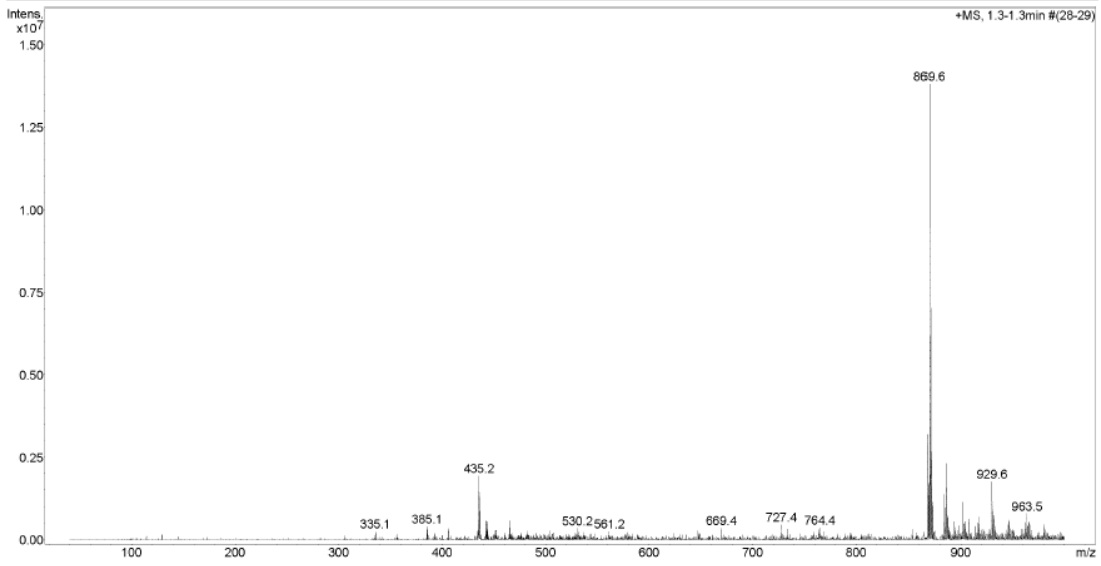
Benutzer: uli

Messung vom: 19/05/2011

Generic Display Report

Analysis Info

Analysis Name	D:\Data\Service_Q1_10\Lehmann_MeBocMc.d	Acquisition Date	1/7/2010 10:38:01 AM
Method	service_ESI.m	Operator	AK
		Instrument	esquire3000 plus
Comment	Lehmann MeBocMc in MeOH + CHCl3		



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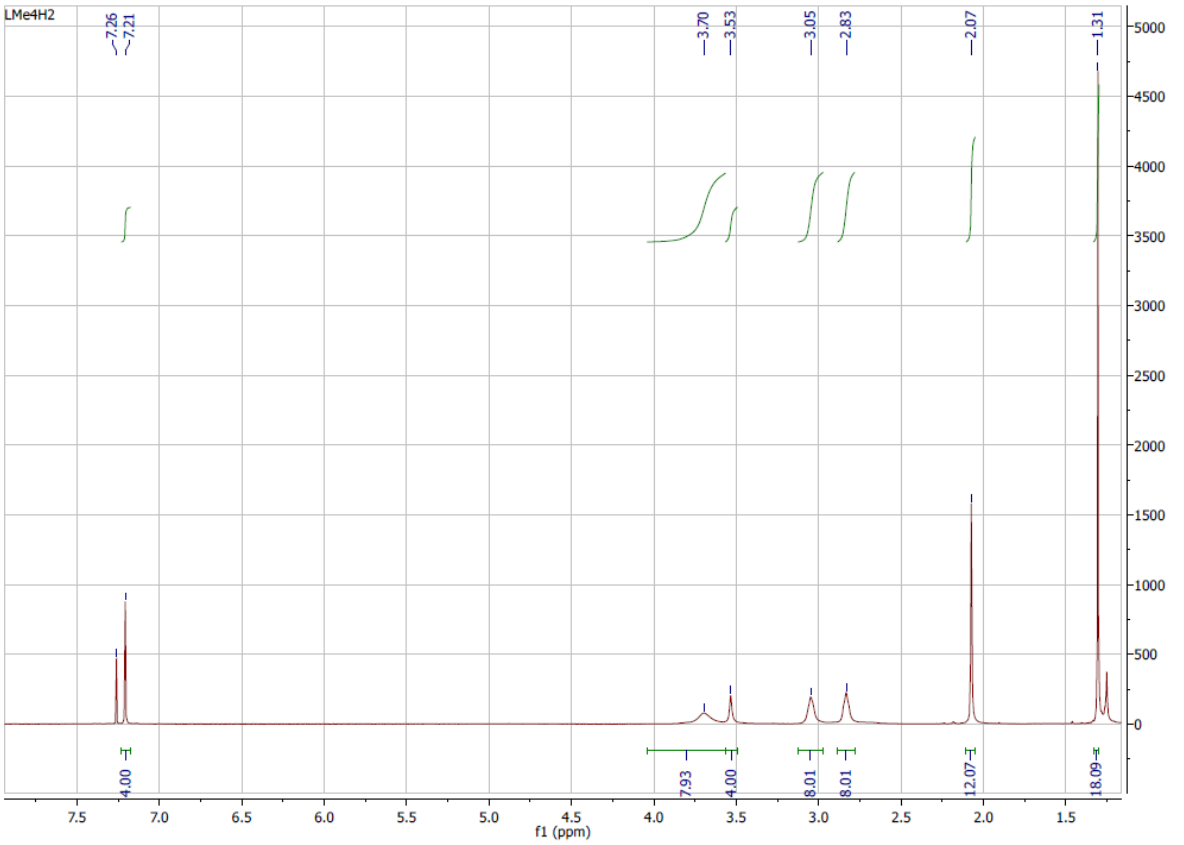
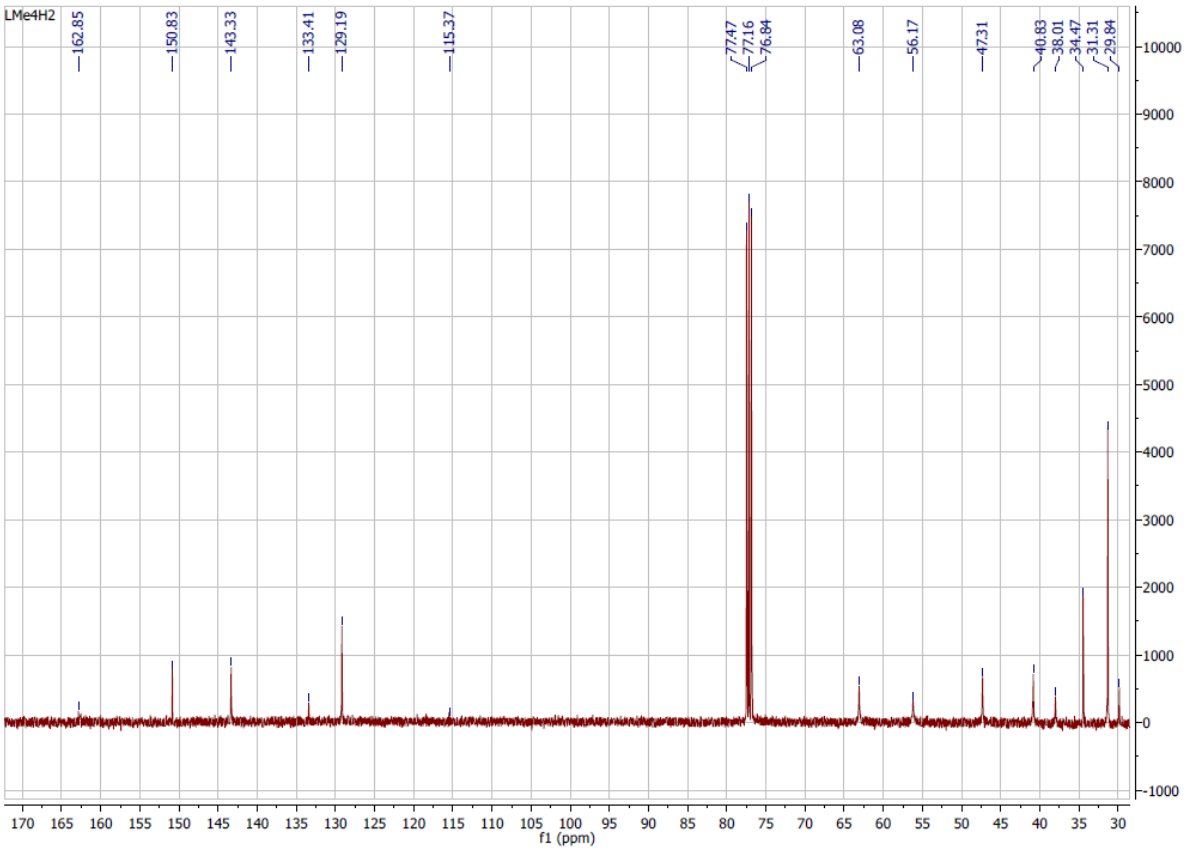
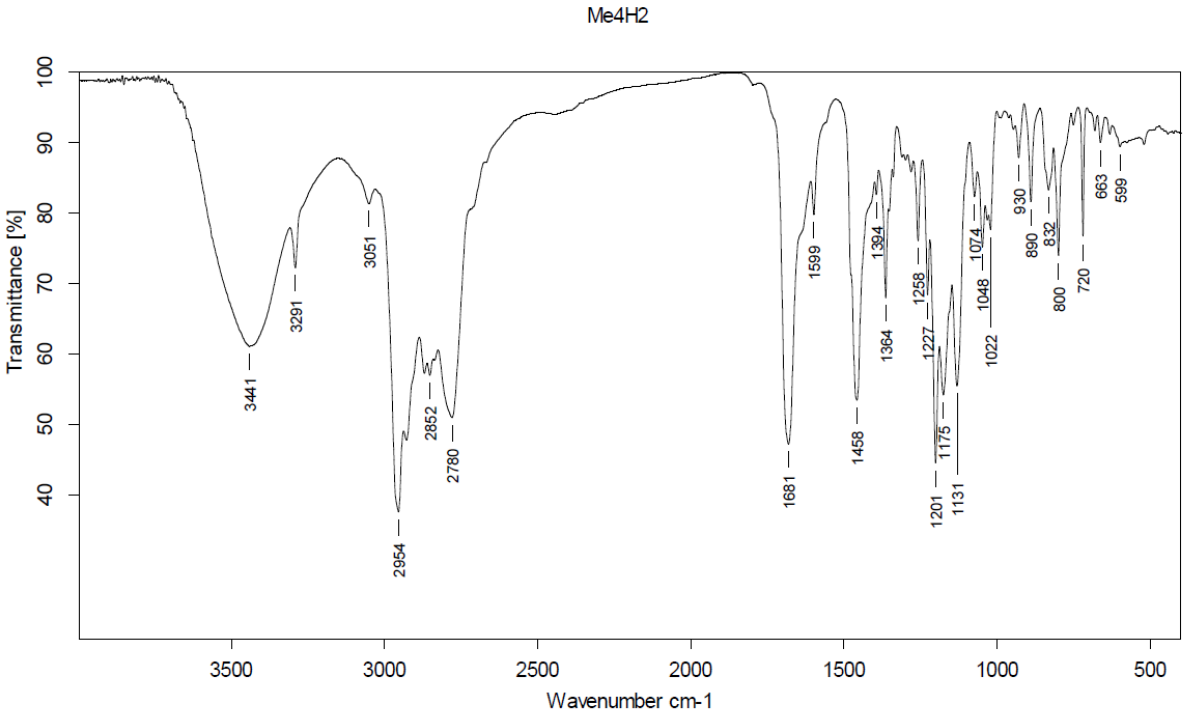
15. Spectra for deprotected macrobicycle **24**.

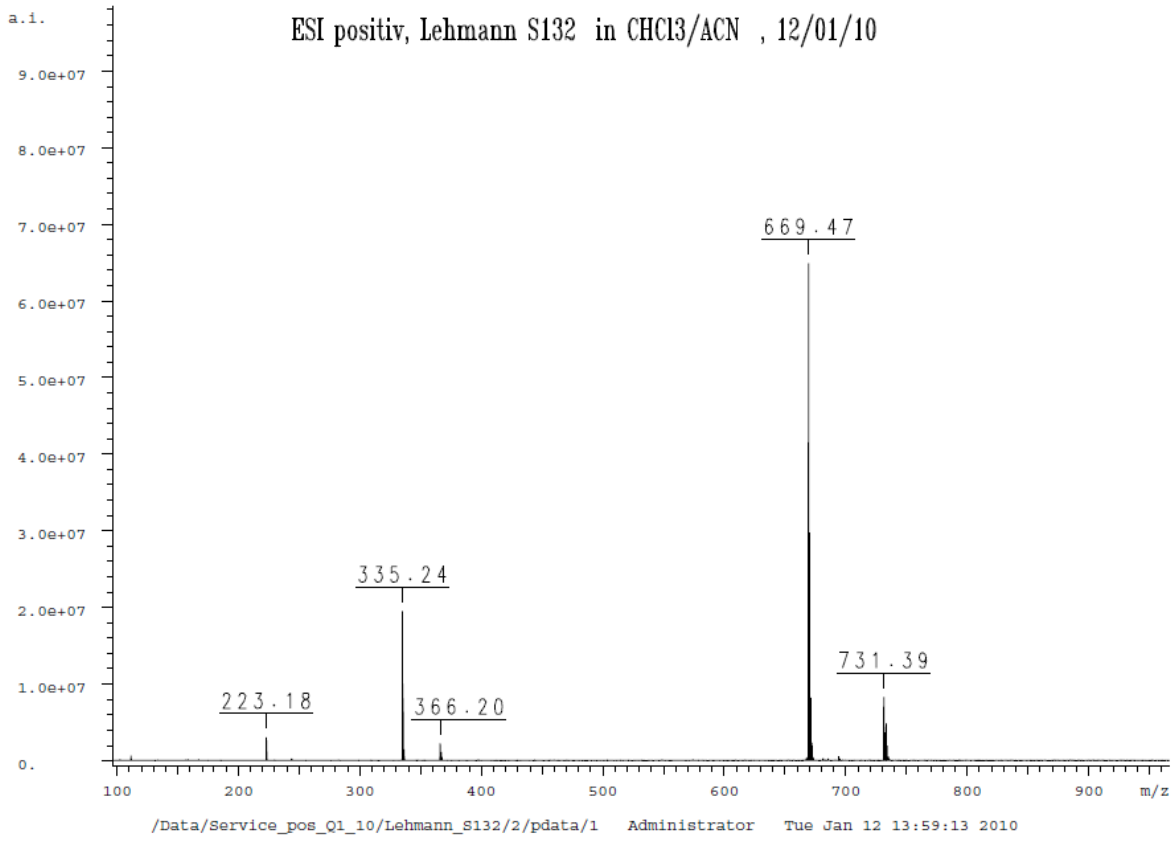


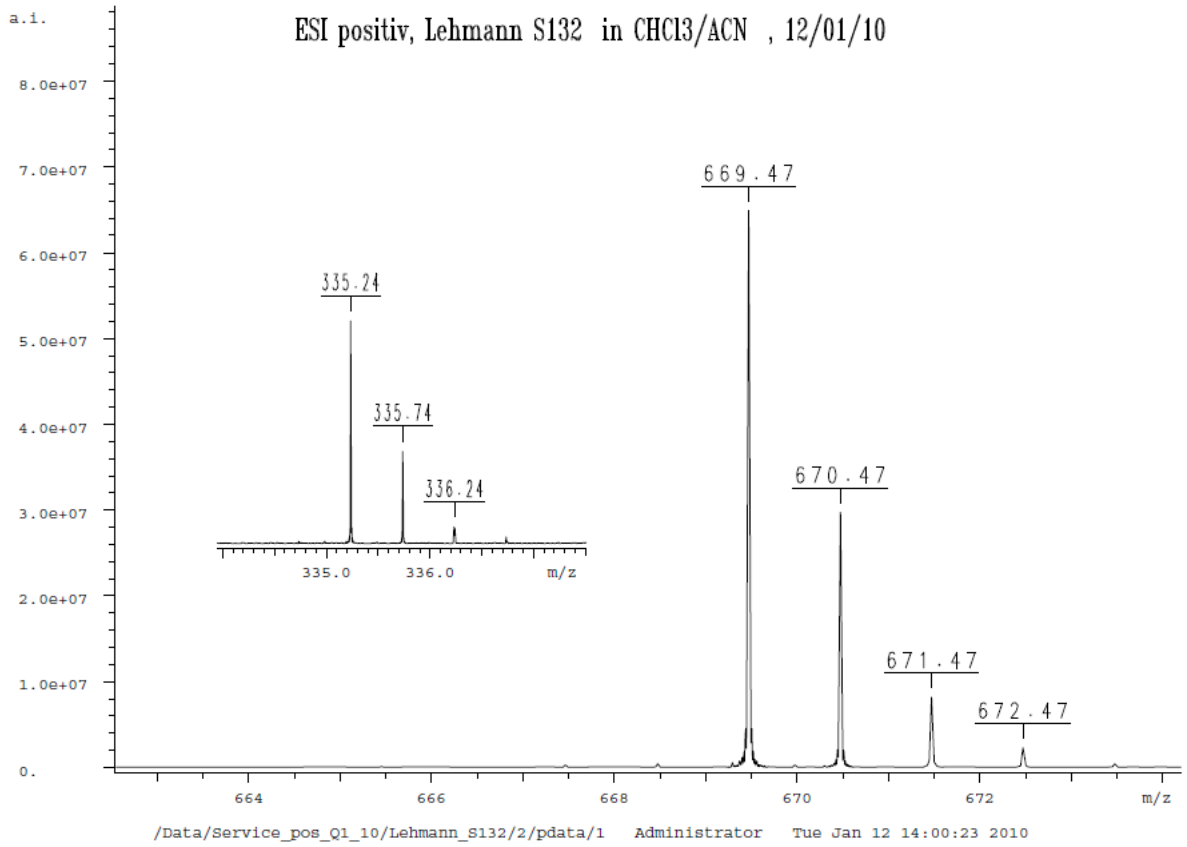




Messxperiment: Standard.XPM

Pfad: C:\IR\Kersting\Uli\BocLigand




ESI positiv, Lehmann S132 in CHCl3/ACN , 12/01/10
a.i.
8.0e+07
7.0e+07
6.0e+07
5.0e+07
4.0e+07
3.0e+07
2.0e+07
1.0e+07
0.
669.47
670.47
671.47
672.47
335.24
335.74
336.24
335.0
336.0
m/z
664
666
668
670
672
m/z
/Data/Service_pos_Q1_10/Lehmann_S132/2/pdata/1 Administrator Tue Jan 12 14:00:23 2010